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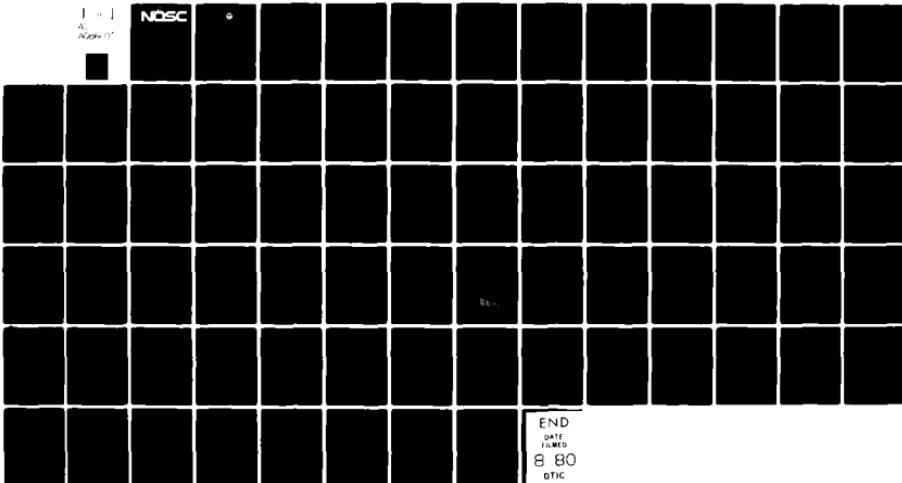
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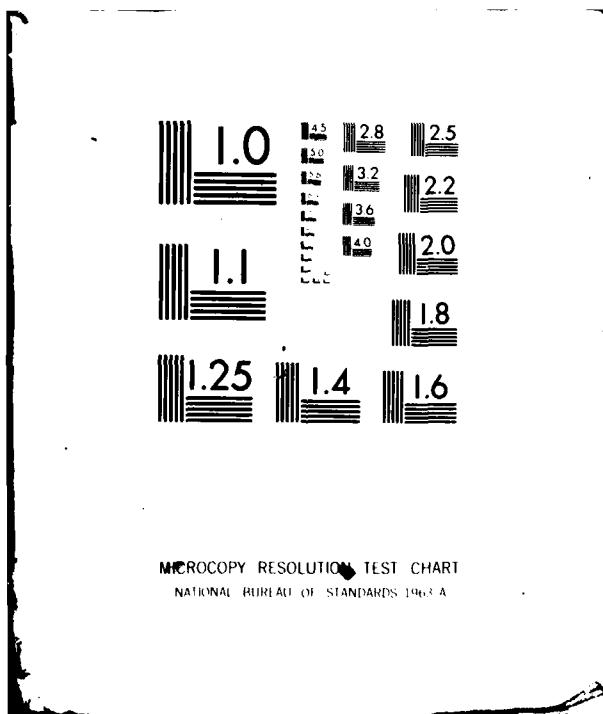
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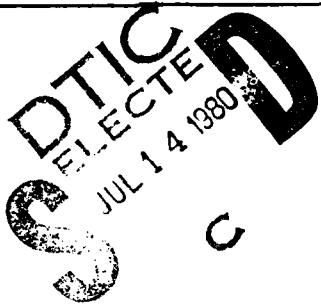
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Technical Report 533

PRODUCTIVITY AND DIVERSITY OF PHYTOPLANKTON IN RELATION TO COPPER LEVELS IN SAN DIEGO BAY

ADA 086660

Sandra M. Krett Lane
San Diego State University Foundation

Final Report: March 1980

Prepared for
Naval Material Command
(MAT 08T24)

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ADMINISTRATIVE INFORMATION

Work on this project was performed by the author while an employee of the San Diego State University Foundation under contract N00123-79-D-0449, task element 61153N, project RR03103, task area 513, work unit ME05, as part of the Marine Environmental Quality Assessment (MEQA) sponsored by the Office of the Chief of the Naval Material Command. Portions of the project were funded also by the Office of Naval Research as part of the "Characterization of Cu, Zn, Pb and Cd in Seawater" project. Dr. Albert R. Zirino, Head, Marine Environment Branch, exercised overall NOSC cognizance.

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ACKNOWLEDGMENTS

The author wishes to thank Dr. Albert Zirino and P. F. Seligman, Naval Ocean Systems Center, for their suggestions and assistance throughout the project, and Dr. Richard Eppley, Scripps Institution of Oceanography, for his advice on nutrient conditions in San Diego Bay.

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NOSC Technical Report 533 TR-533	2. GOVT ACCESSION NO. AD-A086 600	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) PRODUCTIVITY AND DIVERSITY OF PHYTOPLANKTON IN RELATION TO COPPER LEVELS IN SAN DIEGO BAY.		5. TYPE OF REPORT & PERIOD COVERED Final Report, June 1978 - December 1979
6. AUTHOR(s) Sandra M. Krett Lane		7. PERFORMING ORG. REPORT NUMBER 15
8. CONTRACT OR GRANT NUMBER(s) N00123-79-D-0449		9. PERFORMANCE ORGANIZATION NAME AND ADDRESS Naval Ocean Systems Center San Diego, CA 92152
10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61153N, RR03103, 513, ME05		11. CONTROLLING OFFICE NAME AND ADDRESS Naval Material Command (MAT 08T24) Washington, DC 20350
12. REPORT DATE March 1988		13. NUMBER OF PAGES 73
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 16/74		15. SECURITY CLASS. (of this report) UNCLASSIFIED
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited		17. KF03103
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Ecology Phytoplankton Copper San Diego Bay, CA		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Biomass, productivity, and composition of phytoplankton communities were assessed at three sites in San Diego Bay over a period of 1 year. Phytoplankton assemblages taken from regions of low copper levels (less than 1.0 ppb) were characterized by high productivity, biomass and diversity. Samples taken from regions of high copper levels (greater than 3.0 ppb) were less diverse but maintained high biomass and productivity. Phytoplankton tolerance to various copper concentrations was demonstrated by laboratory tests. These findings suggest that the phytoplankton assemblages found in copper-contaminated regions are more tolerant to high copper levels.		

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PROBLEM

Assess biomass, productivity, and composition of phytoplankton communities at three sites in San Diego Bay over a period of 1 year.

RESULTS

Phytoplankton assemblages taken from regions of low copper levels (less than 1.0 ppb) were characterized by high productivity, biomass and diversity. Samples taken from regions of high copper levels (greater than 3.0 ppb) were less diverse but maintained high biomass and productivity. Phytoplankton tolerance to various copper concentrations was demonstrated by laboratory tests. These findings suggest that the phytoplankton assemblages found in copper-contaminated regions are more tolerant to high copper levels.

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INTRODUCTION

In bays and harbors, the major source of copper is copper-based antifouling paints, drainage and waste from manufacturing, dumping activities, and construction (Erickson, 1972; Young *et al.*, 1974; Southern California Coastal Water Research Project, 1976; Zirino *et al.*, 1978). Copper-based antifouling paints have been developed to deter fouling organisms and algal growth on boats and equipment used in the marine environment. Copper is released into the seawater by leaching and by the scrubbing of boat hulls during the removal of accumulated plants and animals. Antifouling paints are estimated to dissolve and leach at a rate of 10-12 micrograms paint/cm²/day (Harvey, 1963). Young *et al.* (1974) calculated that approximately 28,000 gal/year of antifouling paint was applied to commercial, naval, and recreational vessels along the southern California coast in 1973, which represents 50 metric tons of copper. Although it cannot yet be estimated with any reliability what fraction of the copper contained in antifouling paint actually is released to the marine environment, the fact that this toxicant is deliberately added to the paint in a matrix designed to release the toxicant gradually suggests that an important fraction of the copper applied is indeed released to the marine environment before repainting (Young *et al.*, 1974). In addition, during repainting a significant fraction of bottom scrapings may be blown or washed into the harbor water (Young *et al.*, 1974). However, copper introduced in this way may not remain in the water column. Settling and accumulation within the sediments occur if there is little tidal flushing. Chemical precipitation also may take place after contact with seawater.

The availability and toxicity of copper and other trace metals to marine producers depend on metal speciation (Zirino and Yamamoto, 1972; Sunda and Guillard, 1976; Duinker and Kramer, 1977; Gnassia-Barelli *et al.*, 1978). Recent research on chemical speciation in seawater indicates that in natural seawater (pH 8.1), trace metals exist in various forms (Zirino and Yamamoto, 1972). Copper may be complexed, with simple inorganic ligands such as water, halides, carbonate, and sulfate, or it may be complexed by organic ligands such as amino acids, humic acids, sugars, carbohydrates, and polymers (Gnassia-Barelli *et al.*, 1978; Mantoura *et al.*, 1978). Therefore, the total amount of copper available to the phytoplankton and its effect on productivity can be expected to vary greatly with environmental, chemical, and biological conditions.

Since enclosed bays and harbors are more likely to be subjected to increased copper levels (Young *et al.*, 1974), there is now increased interest in the effects of high copper levels on phytoplankton populations found in these areas. As phytoplankton are at the base of the food chain and are highly productive in estuarine regions, possible changes in their productivity because of increased copper levels are of considerable importance in understanding ecological problems of polluted or contaminated areas. A metal that is concentrated in or changes the abundance of primary producers also is likely to have indirect effects on higher trophic levels.

San Diego Bay is an enclosed body of water that is subject to possible copper contamination because of the considerable amount of marine traffic. For example, the U.S. Navy maintains a major portion of the Pacific Fleet in the central and southern portions of the bay; there is substantial use of San Diego Bay by commercial vessels; and thousands of private boats are docked at both private and public marinas. Variations in copper concentrations throughout San Diego Bay have been documented by Zirino *et al.* (1978). One site is an area on the western side of Shelter Island, where a large portion of San Diego's privately owned pleasure and fishing vessels is docked. Their data indicate that the total copper concentration in this area is much higher than in other areas of San Diego Bay. The concentration may reach

11.0 ppb in the Shelter Island region, compared with 2.0 to 4.0 ppb in other regions of the bay. Fluorescence measurements of phytoplankton chlorophyll taken in this area at the same time as copper measurements indicated the presence of dense phytoplankton populations (Zirino, personal communication).

This relationship is contrary to the expected. Current research indicates that copper concentrations as low as 1.2 ppb are toxic to some species of phytoplankton (Steeman, Nielsen and Wium-Andersen, 1970, 1971; Saifullah, 1978). Therefore, one might expect that the phytoplankton community in this area would not be very dense unless other factors were operating to mask the effects of high copper concentrations.

The biological and chemical factors involved in this high copper-dense phytoplankton relationship are not fully understood. Such a relationship has been observed by other investigators in both laboratory studies (Mandelli, 1969; Erickson *et al.*, 1970) and in field situations (Russell and Morris, 1970; Steeman, Nielsen, and Laursen, 1976; Foster, 1977). Several hypotheses have been developed to explain why phytoplankton are able to withstand elevated levels of copper. The chemical speciation of the copper may be such that it is made unavailable and thus nontoxic to the phytoplankton (Steeman, Nielsen and Wium-Andersen, 1970); the phytoplankton populations may be composed of species that can tolerate high concentrations of copper (Thomas and Seibert, 1977; Thomas *et al.*, 1977); bacteriological activity may change the nature of the complexed copper (Vaccaro *et al.*, 1977), or the high copper levels may adversely affect predator populations (Beers *et al.*, 1977) which, in turn, results in increased phytoplankton populations.

These hypotheses suggest that the factors regulating the copper-phytoplankton relationship in one region may be different from those regulating this relationship in another. Therefore, it is important that when such a relationship is observed, it must be studied in depth; and that the biological, chemical, and physical trends characteristic to that environment be quantitatively determined. These trends and relationships may then be extrapolated to other areas experiencing trace metal contamination.

The purpose of this investigation was to determine whether natural phytoplankton communities are affected by elevated ambient concentrations of copper in San Diego Bay, California. Emphasis was placed on determining whether changes in biomass, productivity, or diversity could be associated with elevated copper levels. The physical and chemical properties characteristic of the area were determined from regular measurements. An effort was made to determine whether there are any significant correlations between the physico-chemical features, copper levels, and phytoplankton community attributes. The tolerance of phytoplankton communities from contaminated and noncontaminated habitats was examined and estimated in a controlled laboratory experiment. The majority of phytoplankton toxicity or tolerance tests conducted by other investigators have involved monocultures of phytoplankton and synthetic culture media. The relationships under investigation permit natural phytoplankton communities to be utilized in their respective seawater environments.

MATERIALS AND METHODS

FIELD SAMPLING

Samples for this study were collected from three representative areas within San Diego Bay (figure 1). A "control" site was located at the Shelter Island fishing pier, on the east side of Shelter Island. The first test site was located on the west side of Shelter Island

at the "Tonga 76" docking facilities. The second test site was located at the U.S. Navy pier 6, 32nd Street Naval Shipyard, in the inner portion of San Diego Bay. Maximum water depths were 13, 15, and 22 feet for the "control," first test site, and second test site, respectively.

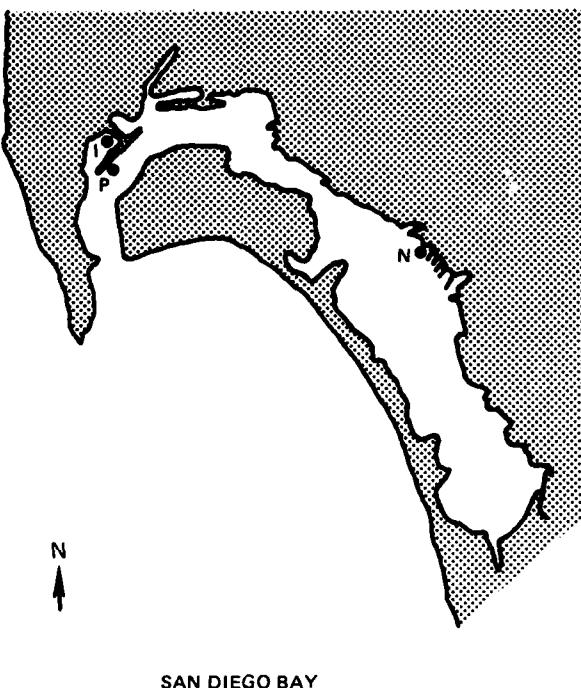


Figure 1. Field sites monitored within San Diego Bay, California, from July 1978 through June 1979. P = PIER site, I = INLET site, N = NAVY site.

The fishing pier location (now referred to as PIER) was selected as the "control" because it lacked heavy boat traffic, had good tidal flushing, and its copper concentrations were similar to other unpolluted areas of San Diego Bay. This control site was near enough to the first test site to allow near-simultaneous sampling yet distant enough not to be contaminated by the boats harbored on the west side of Shelter Island.

The first test site (now referred to as INLET) was chosen because it was previously described by Zirino *et al* (1978) to be high in copper and, contrary to what might be expected, high in algal fluorescence.

The U. S. Navy pier 6 site (now referred to as NAVY) was included in this study because it is an area where large-scale ship maintenance is performed in a relatively clean, enclosed body of water. This site is of ecological interest because it is located in the southern region of San Diego Bay, where tidal flushing is reduced. Therefore, one might expect the effects of elevated copper levels to be more pronounced there.

The three sites were monitored for a period of 1 year. Sampling was initiated on 17 July 1978 and concluded on 6 June 1979. Samples were taken between 0700 and 0900 hours at approximately 1-month intervals during the year. Three intensive sampling sessions were performed to observe daily and hourly variations in phytoplankton dynamics in

relation to sunlight and tidal conditions. An intensive sampling session consisted of collecting six samples on 4 consecutive days. Three samples were taken on consecutive days between 0700 and 0900 hours. The other three samples were taken on the fourth day at 0700, 1200, and 1600 hours. These sampling sessions were performed during August and November 1978 and February 1979.

A total of 31 samples was collected at each site over the 1-year period. Because of a lack of personnel, samples were not taken at the NAVY site on 30 August 1978, 28 November 1978, 21 February 1979 (0700 hours), and 21 February 1979 (1600 hours).

Water samples were taken as "integrated samples" from the surface to a depth of 1 m below the surface with a 6-l Niskin sampling bottle. A 6-l sample was then subdivided into ten 250-ml samples to be used for copper analysis, phytoplankton identification, chlorophyll extractions, salinity, and pH determinations, with three 50-ml samples taken for nutrient determinations. A 4-l polyethylene bottle was also filled with water to be used for productivity measurements and particulate analysis. This second water sample was collected at the same time as the Niskin bottle sample.

All sample bottles used in this study were constructed of polyethylene. They were prepared by soaking in 8N HNO₃ for at least 16 hours. After soaking, the bottles were rinsed three times with Milli-Q distilled water, which is purified by a Millipore system consisting of an activated carbon cartridge to remove dissolved organics, two deionization cartridges to remove dissolved inorganics, and a Millipore membrane filter unit to remove microorganisms and particles smaller than 0.22 μ . Water purified by this system was analyzed for copper concentration by atomic absorption spectroscopy. The results of weekly measurements indicated copper levels to be less than 0.1 ppb.

Seawater samples were identified by the code AB, where A designated the sample number (1-31) and B designated the sample site (P for PIER, I for INLET, and N for NAVY). Thus a sample with the identification 10P is the 10th sample from the PIER site.

Time, seawater temperature (measured with a glass laboratory thermometer), and general weather conditions were noted at the time of sample collection. In the laboratory, the pH of the seawater was measured with a Horizon pH meter. The salinity of the sample was determined on a Beckman model RS-7B portable induction salinometer. These measurements were made within 24 hours after sample collection.

PRODUCTIVITY DETERMINATIONS

Primary productivity of natural phytoplankton populations was determined by ¹⁴CO₂ uptake. The methods used are those outlined in Standard Methods for the Examination of Water and Wastewater (American Public Health Association, 1975), with few minor changes.

In the laboratory, and within 1 hour of the time samples were taken, two light and one dark 300-ml BOD bottles were filled with the sample water from each site. Each bottle was inoculated with 1 microcurie of Na¹⁴CO₃. The bottles were then placed in an incubator for four hours at 18°C and 978-1400 microwatts/cm². Light was measured as irradiance by means of a United Detector Technology model 21A power meter. A filter was used to maintain a flat response between 400 and 900 nm. After the incubation period, two 100-ml samples were taken from each bottle and filtered through 0.45-micron Millipore filters. A 10-ml rinse of 0.001 N HCl in 3% NaCl in distilled water followed the filtration (Strickland, 1960; Kahlisco, 1964). This rinse removed excess ¹⁴C from the outside of the plankton cells.

The filter was then put into a scintillation vial which contained 10 mL of Aquasol liquid scintillation fluor.

Twenty-four hours was allowed to elapse before the samples were counted to assure complete disassociation of the particulate material from the filter. The samples were counted with a Nuclear Chicago Unilux III liquid scintillation counter. Samples were counted for two minutes in the presence of two standards consisting of fluor, filter, and known volumes of ^{14}C . This method was used in preference to the external standard method because there appeared to be a great deal of quenching with the filter in the sample.

Carbon uptake was determined by the following expression (Standard Methods, 1975):

$$\begin{aligned} \mu\text{g C fixed/L/hour} &= \frac{\text{counts/minute}}{\text{added activity}} \times \frac{\text{volume incubated}}{\text{volume filtered}} \\ &\quad \times \text{carbon} \times \frac{1.064}{\text{hours incubated}} \end{aligned}$$

where counts/min = mean dark bottle sample counts subtracted from the mean light bottle counts for each replicate pair

$$\text{Added activity} = 2.2 \times 10^{-6} \text{ microcuries}$$

$$\text{Carbon} = \text{carbonate alkalinity (CA)} \times 0.90 \times 12 \times 10^6$$

$$\text{CA} = \text{titration alkalinity (TA)} - 0.00008$$

$$\text{TA} = 12.3 \times \text{salinity}/1.80655 \times 0.00001.$$

Carbon, CA and TA were determined by means of the equations given by Harvey (1963).

CHLOROPHYLL A EXTRACTIONS

Three amber 250-mL sample bottles were filled at the sample site for chlorophyll A determinations. These measurements were conducted within 2 hours after sample collection. The samples were kept in the dark at 18°C until time of analysis. The procedures used for chlorophyll A extractions are given in Seligman (1974). A summary of the methods is as follows.

A 100-mL aliquot was taken from each of the amber sampling bottles, which resulted in three replicate samples per site. These were filtered by means of Whatman GF/C, 2.25-cm-class filters. A layer of 1% (w/v) MgCO_3 was added to the filter (1 mL) prior to filtration. After filtration of the 100-mL sample, the filter and trapped particulate material were placed in 8 mL of 90% (v/v) acetone and were sonified for 1.5 minutes in an ice bath by means of the microtip attachment on a Heat Systems sonifer cell disruptor. After sonification, the calibrated centrifuge tubes were filled to 10 mL with the 90% acetone, stoppered, and placed in the dark for a minimum of 10 minutes. After extraction of the pigments was complete, the sample was centrifuged for 10 minutes on an International Clinical centrifuge. The supernatant was then decanted into a 5-mL fluorometer cuvette. Fluorescence was measured on a Turner Model III fluorometer. An initial value of fluorescence (F_0) was recorded, followed by the addition of 1 drop of 4 N HCl. After 1 minute, a second reading (F_a), representing the phaeophytin value, was recorded. Chlorophyll A concentrations were determined according to Holm-Hansen *et al* (1965) by means of the following formula:

$$\text{Chl A (mg/m}^3\text{)} = \frac{9.292 \times (F_0 - F_a)}{\text{liters filtered}}.$$

PRODUCTIVITY INDEX

To measure the fertility of a phytoplankton assemblage and its endemic crop of phytoplankton, the productivity index can be determined. This is given by Strickland (1960) as the ratio of cell carbon/chlorophyll A. The productivity index allows the comparison of phytoplankton assemblages from different regions since it takes into account both the density of phytoplankton and the rate of photosynthesis of that assemblage. In this work the index is calculated as

$$\text{Productivity index} = \frac{\mu\text{g carbon uptake/l/hr}}{\text{mg chlorophyll A/m}^3}$$

to yield an index in terms of carbon uptake/chlorophyll A/hour.

PLANKTON IDENTIFICATION

During sample collection, 10 mL of 40% (v/v) formalin (pH approximately 8.5) was added to two 250-mL samples from each site. Back in the laboratory, approximately 0.1 mL of Rose Bengal stain was added to each bottle. Rose Bengal is a stain specific to protoplasm (A. Dodson, personal communication), and thus facilitates the recognition of "live" phytoplankton from detrital material. From these stained samples, two 100-mL settling chambers were prepared. The samples were allowed to settle for at least 24 hours. Plankton was identified to the level of genus. The number of cells of each genus present was recorded. A Wild inverted phase microscope was used for plankton identification. Taxonomic keys of Cupp (1943) and Yamaji (1962) were used for these identifications. From the counts obtained during microscopic examination, the densities (number of organisms/l) were estimated.

DIVERSITY INDEX

Hurlbert's probability of interspecific encounter (PIE) index (as described by Cox, 1967) was used to describe diversity of each community. This index corresponds to the proportion of encounters among individuals of one species moving in a random manner that involve individuals of different species (Cox, 1967). Therefore, it takes into account the number of species (or genera), the total number of individuals of all species (genera), and the number of individuals of the i^{th} species (genus). This index ranges from 0 to a maximum of 1.0 for a highly diverse community.

ANALYSIS OF COPPER IN PARTICULATE MATERIAL

To determine the amount of copper in particulate material, three 500-mL samples of seawater from each site were filtered through 0.45- μ Millipore filters of 47-mm diameter. The weight of this particulate material was determined by the following procedure:

1. Prior to filtration, all filters were dried in a microwave oven and stored in a desiccator.
2. The dry weight of the filter was determined.

3. After filtration, the filter and the particulate material retained on the filter were again dried in a microwave oven and stored in a desiccator.
4. The filter and particulate material were reweighed and the weight of the filter was subtracted from the combined weight of the filter and particulate material to yield the particulate weight.

Although precautions were taken to avoid errors in weight measurements, a few instances of negative particulate weights were encountered. This probably was the result of incomplete drying of the filter itself prior to filtration.

The particulate material was then analyzed for copper by means of X-ray fluorescence. An Ortec Tefa model 6110 X-ray fluorometer was used in conjunction with a PDP-11 minicomputer. The samples were analyzed under the following conditions:

Anode current	200 μ A
Anode voltage	50 kV
Detector	SiLi
Filter	Mo
Anode	Mo
Energy scale	20.48 keV
Time	1000 s.

Calibration of Intensity

X-ray fluorescence spectrophotometry is used to determine the concentration of a given metal in a sample as intensity of emitted X-rays in counts/second. These intensities need to be calibrated for the analyte metal in a given matrix. To calibrate intensities for copper levels in particulate material, a series of particulate samples was analyzed by X-ray fluorescence spectrophotometry and the intensities were calculated by the computer. Specific samples were selected from this series to represent a wide range of intensities. These selected samples were then digested with HNO₃ and analyzed by atomic absorption spectroscopy. The copper levels in μ g Cu were determined for the particulate material. These data were paired with the respective intensity data and entered into the computer. A linear regression analysis was performed and a regression equation determined.

Determination of Copper in Particulate Material

The particulate samples for this study were analyzed as previously described. The intensities calculated by the computer were then used in the regression equation to calculate copper concentrations as μ g Cu. From this value, levels of copper/l seawater were then determined.

ANODIC STRIPPING VOLTAMMETRY

Seawater samples can be measured directly for trace metal content by anodic stripping voltammetry (ASV) (Zirino and Kounaves, 1978). ASV is an electrochemical method that allows rapid and accurate determination of trace metal concentrations of less than 1 ppb without pretreatment or preconcentration of the sample. It has the advantage over classical wet methods of trace element analysis that few errors are introduced during analysis through contamination from glassware, chemical reagents, and concentration techniques (Whitnack and Sasselli, 1969).

The basis for ASV is described by Copeland and Skogerboe (1974). In general, the measurement involves two discrete steps: the analytical species is reduced (electroplated)

onto the working electrode and is then stripped back into the solution. At the oxidation potential of each analytical species, the faradaic current produced is thus stripping current as a function of the electrode (oxidation) potential. The stripping current resulting from oxidation of each analyte is proportional to the concentration of that analyte in the electrode, and thus in the solution.

A Princeton Applied Research (PAR) 315 automated electroanalysis controller was used in conjunction with a PAR 174A polarographic analyzer. A Hewlett Packard 7034A X/Y recorder was used to give a permanent readout of the stripping current. The electrodes and cell used during this study are similar to those described by Zirino and Kounaves (1978). The cell vessel was constructed of glass. The vessel fit onto a PAR No. 9300 polarographic top. The seawater sample was stirred with a 1.1-cm Teflon-covered stirring bar coupled to a Sargent-Welch 600-rpm synchronous-speed magnetic stirrer. A Beckman fiber-junction saturated-calomel electrode (SCE) was used as reference while a platinum foil wound around the SCE served as the counterelectrode. A hanging mercury drop electrode (HMDE) served as the working electrode. All samples were analyzed at room temperature.

The conditions under which the samples were analyzed for copper are as follows:

- Differential pulse mode.
- Potentials: conditioning = 0, deposition = -0.9, final = +0.1.
- Deposition time: 300 s.
- Scan rate: 5 mV/s.
- Drop size: 4 divisions.
- Sample volume: 25 mL.
- Purge: 300-ppm CO₂ in nitrogen – 5 minutes initial, 1 minute between standard additions.
- Copper standard: 1000 ppb Cu in Milli-Q distilled water with 0.1% HNO₃ added to prevent absorption onto the container walls.

The concentration of copper in the seawater sample was determined by comparing the peaks produced during the stripping phase of analysis of the sample to the peaks produced by the sample plus standard addition. Linear regression analysis was used.

ANALYSIS OF COPPER IN SEAWATER

Copper in seawater was measured by ASV under three conditions: pH 8 (natural pH), pH 2 (adjusted), and pH 2 filtered. Each condition yields a portion of the total amount of copper characteristic to the sample. The theory behind detectable copper is given by Zirino (personal communication). Measuring the sample at pH 8 (or ambient pH) yields the portion of copper that is in solution and available for phytoplankton interaction. By acidifying the unfiltered sample to pH 2, copper that is complexed with highly inert inorganic ligands and organic ligands not measurable at pH 8 is disassociated and now detectable. In theory, this concentration should approximate the "total" copper concentration in the seawater sample. The fraction of copper complexed to colloidal substances can be determined by first filtering the seawater and then acidifying the sample to pH 2. The acidification releases copper that is bound to colloidal material that passes through filtration. Ten microliters of concentrated HCl was used for the acidification of the seawater samples.

Seawater was filtered for the determination of copper by the following procedure:

1. A Millipore filter apparatus (funnel, neck, and bottle) was rinsed with clean 8 N HNO₃.
2. The apparatus was then rinsed three times with Milli-Q distilled water.
3. To remove the effects of acidification from the nitric acid rinse, the apparatus was rinsed with "clean" filtered seawater (copper level previously determined to be less than 1.0 ppb).
4. 0.45-micron Millipore filters were used to filter the test seawater. These filters were rinsed with Milli-Q distilled water, but not with acid prior to sample filtration.
5. After filtration of each sample, the filter was discarded, the filtrate poured back into the sample bottle which had been rinsed with a small aliquot of filtrate, and the apparatus then rinsed with Milli-Q distilled water.
6. Steps 4 and 5 were repeated until all samples being analyzed at a given time (generally a set of three samples) were filtered.
7. The entire procedure was repeated for each batch of samples.

NUTRIENTS

The seawater samples were analyzed for nitrate (NO₃), nitrite (NO₂), phosphate (PO₄), and silicate (SiO₄). The samples were taken at the time of seawater collection and frozen upon returning to the laboratory. The samples were then taken to the San Diego State University Ecology Laboratory, where they were analyzed on a Technicon Auto Analyzer II. The values were reported in terms of $\mu\text{g-at nutrient/l}$.

LABORATORY TEST TO DETERMINE THE TOLERANCE OF NATURAL PHYTOPLANKTON ASSEMBLAGES TO ELEVATED COPPER LEVELS

It has been suggested by many investigators (Stokes *et al.*, 1973; Harrison *et al.*, 1977; Thomas *et al.*, 1977; Thomas and Seibert, 1977) that phytoplankton inhabiting areas of relatively high copper levels are more tolerant to increasing levels of copper than are phytoplankton inhabiting areas of low copper levels. This tolerance is generally observed to exist in a few species which, under prolonged exposure to high copper levels, become the dominant species (Thomas *et al.*, 1977).

Copper measurements made at the three field sites in San Diego Bay for nine months (July 1978 through March 1979) indicated that the level of ambient copper at the INLET site was higher than at the PIER (control) site. A laboratory test was developed to assess the tolerance of the phytoplankton from the PIER and INLET sites to elevated levels of copper. The experimental procedure used was essentially the same as that of Harrison *et al.* (1977) and consisted of a 24-hour incubation of natural assemblages of phytoplankton in seawater containing varying concentrations of copper. The assemblages incubated at each copper level were assessed for productivity, chlorophyll A concentration, and diversity among genera. Seawater samples were analyzed for soluble, colloidal, and total copper levels.

Eight liters of surface water (0- to 1-m depth) was collected from the PIER and INLET sites on 11 April 1979 at 0800. The water was immediately brought to the laboratory where 500-mL aliquots were transferred into 500-mL Erlenmeyer flasks. These flasks, and all other glass and plastic ware used in this experiment, were soaked for 18 hours in 8 N HNO₃, rinsed three times with Milli-Q distilled water, rinsed twice with "clean" (less than 1 ppb copper) filtered seawater from Point Loma, and then rinsed once with the test water.

Five copper concentrations were used in this study. These were ambient, as well as ambient +5, +10, +20, and +50 ppb copper. Each concentration assessed was prepared in triplicate to avoid possible error from glassware contamination or error in laboratory procedure.

After the 500 mL of test seawater was transferred into the Erlenmeyer flasks, appropriate amounts of cupric-sulfate (Baker Analyzed Reagent Grade) dissolved in Milli-Q distilled water were added to the seawater to yield the predetermined copper levels. After inoculation, the flasks were placed in a Precision Scientific model 808 constant-light and constant-temperature incubator for 24 hours.

Following the preincubation period, subsamples were withdrawn from each flask for ^{14}C productivity measurements (three 50-mL aliquots), chlorophyll A determinations (three 25-mL aliquots), copper determinations (50 mL each for soluble, colloidal, and total copper), and phytoplankton identification (two 50-mL aliquots). The ^{14}C labeled samples were then incubated for 3.5 hours under constant light and temperature conditions. This and each of the other tests were carried out by means of the same methods described for regular monthly sampling.

Samples were identified by the following code: X-Y-Z, where X designated the site (either P for PIER or I for INLET), Y designated the copper level added to the ambient seawater (0, 5, 10, 20 or 50), and Z designated the replicate number (1, 2, or 3). This identification scheme will be used to refer to samples from the laboratory experiment.

STATISTICAL ANALYSIS

Multiple Partial Correlation Analysis

In an effort to determine whether there were correlations between copper levels and phytoplankton productivity and community composition, a multiple partial correlation analysis was completed for the following variables: temperature, salinity, tidal position, pH, primary productivity, chlorophyll A, productivity index, diversity in genera, copper associated with particulates, soluble copper, colloidal copper, total copper, estimated total copper, and particulate material/L. Estimated total copper is equal to soluble plus colloidal copper concentrations. All analyses were evaluated at the 5-percent level of significance.

The requirement for correlation analysis is that the data be normally distributed. To test for normality among the variables, a Lillifores test for normality (Conover, 1971) was performed on each variable. Those variables not meeting the requirement were transformed. Log transformations [$\log(x + 1)$] were first performed on these data. If the log transformations were not successful at obtaining normality, then square-root transformations (\sqrt{x}) were performed. In all cases but one, copper associated with the particulate material at the INLET site, the transformations were successful.

The partial correlation was performed on all samples taken during the morning sampling period, thus excluding those noon and afternoon samples taken on 30 August 1978, 27 November 1978, and 21 February 1979. A total of 25 samples were correlated from the PIER and INLET sites, and a total of 23 were correlated from the NAVY site.

A second correlation was performed on the characteristics measured for phytoplankton (productivity, chlorophyll A, productivity index, diversity of phytoplankton), copper measurements (soluble, colloidal, total, total minus soluble, and particulate copper), and nutrients (PO_4 and SiO_4). Physical measurements were not included in this correlation.

Randomized Block Analysis of Variance by Ranks

To determine whether the copper levels and the phytoplankton characteristics measured at the three sites were significantly different from each other, the Friedman randomized block analysis of variance by ranks was performed on the data. In cases where the Friedman test indicated a significant difference, the nonparametric multiple comparison test was then used to determine which of the three sites was significantly different from the others. Nonparametric analyses were used in all cases as the data did not meet the criteria of normality for parametric analyses. All of these analyses were evaluated at the 5-percent level of significance.

RESULTS

COPPER-SOLUBLE FRACTION

The soluble fraction of copper in seawater was measured by anodic stripping voltammetry under pH 8, unfiltered conditions as described above in the methods section. The levels of copper measured at the three sites over the year are presented in figure 2. Analysis of these data by the Friedman test, followed by the nonparametric multiple range test, indicates that the concentration of copper at the PIER site was significantly lower than copper levels at both the INLET and NAVY sites (p values < 0.05). There were no other significant differences among sites (p values > 0.05). The data in figure 2 indicate that the soluble fraction of copper at the PIER site exceeded 1.0 ppb only on two occasions, and that it frequently was below the 1.0-ppb level.

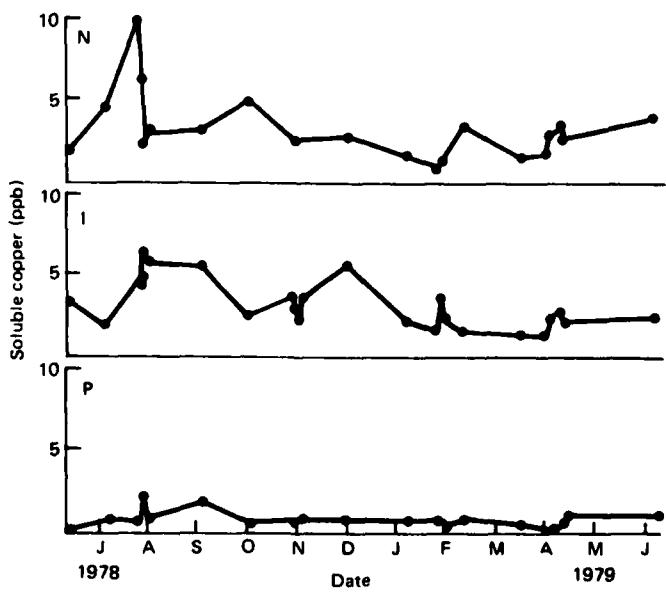


Figure 2. Trends in soluble copper (ppb) at the PIER (P), INLET (I), and NAVY (N) sites from July 1978 through June 1979.

However, the soluble fraction of copper at the INLET and NAVY sites rarely fell below 2.0 ppb and frequently exceeded 6.0 ppb. At all three sites, levels were slightly elevated during late summer and early fall. The individual values obtained for soluble copper in seawater at the PIER, INLET, and NAVY sites over the year are given in appendix table 3.

TOTAL COPPER

The total concentration of copper in seawater was measured by anodic stripping voltammetry at pH 2 under unfiltered conditions, as described in the methods section. The levels of total copper measured at the three sites over the year are presented in figure 3. Individual total copper levels measured for the PIER, INLET, and NAVY sites over the year are also given in appendix table 3.

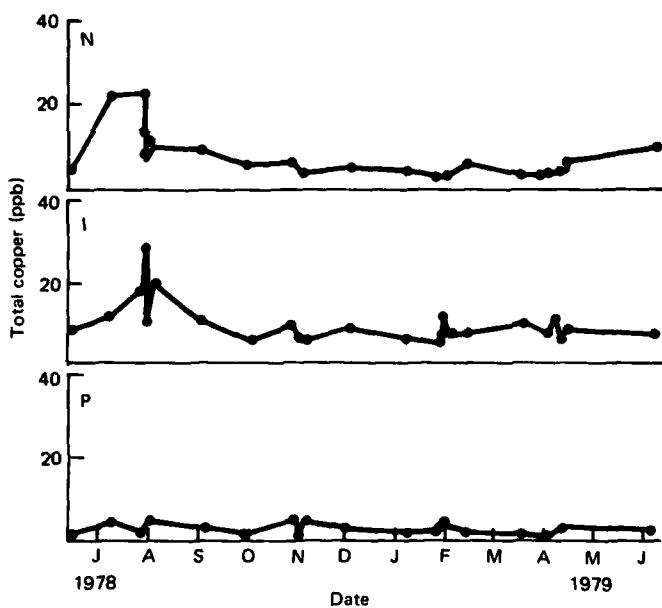


Figure 3. Trends in total copper (ppb) at the PIER (P), INLET (I), and NAVY (N) sites from July 1978 through June 1979.

Total copper at the PIER site remained below 4.0 ppb throughout the year, with the majority of measurements concentrated around 1.5 ppb. Major fluctuations within the total copper measurements occurred during early August 1978 (4.0 ppb) and November 1978 (3.1 ppb).

Total copper levels at the INLET and NAVY sites were higher than encountered at the PIER site. The results of a Friedman test, followed by the nonparametric multiple range test indicate that the total copper levels maintained at the PIER, INLET, and NAVY sites all were significantly different from each other (p values < 0.05). Total copper levels ranged between 5.1 and 14.2 ppb at the INLET site and 2.2 and 22.6 ppb at the NAVY site. The highest total copper levels occurred during late summer and early fall at both the INLET and

NAVY sites, leveling off to concentrations of approximately 8.0 ppb at the INLET and 6.5 ppb at the NAVY sites during spring and early summer.

COPPER ASSOCIATED WITH COLLOIDAL MATERIAL

The amount of copper present which is associated with colloidal material can be estimated by the acidification of filtered seawater. Although this procedure yields estimates of both colloidal and soluble copper concentrations, this fraction will be referred to as the colloidal fraction.

The levels of colloidal copper measured at the three sites over the year are shown in figure 4. The individual values also are given in appendix table 3.

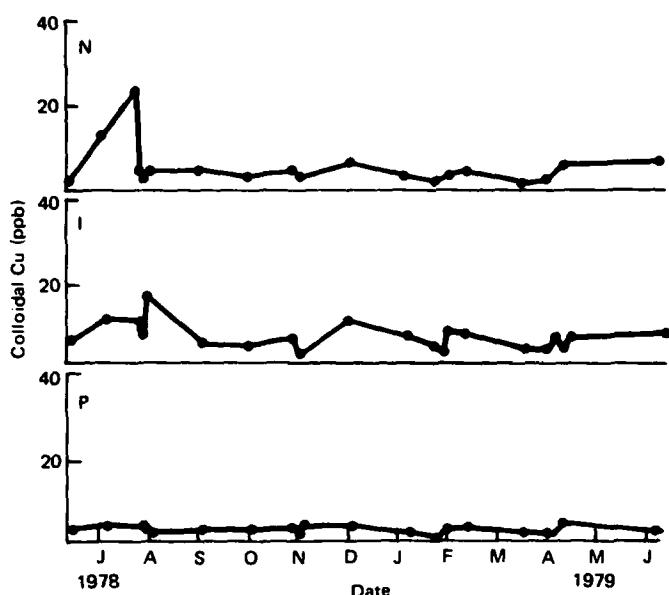


Figure 4. Trends in colloidal copper (ppb) measured at the PIER (P), INLET (I), and NAVY (N) sites from July 1978 through June 1979.

The colloidal fraction of copper measured at the PIER site was much lower than those encountered at the INLET and NAVY sites. However, the results of a Friedman test, followed by a nonparametric multiple range test indicate that the fraction of copper associated with colloidal material was significantly different among all three sites (p values < 0.05).

The PIER site is characterized by colloidal copper levels varying slightly around a concentration of 1.5 ppb. Levels of colloidal copper at the INLET site fluctuated considerably around a level of 5.8 ppb. Extreme high concentrations of 8.3 to 14.1 ppb copper in the colloidal material were encountered during late August 1978. Another significant elevation in these measurements occurred during late February 1979. Low levels of colloidal

copper occurred during the fall (1.2 to 3.3 ppb) and during the spring (2.9 and 4.1 ppb). High levels were observed during the summer months.

The colloidal copper levels measured at the NAVY site followed a pattern similar to the INLET site. Extreme high levels were encountered during August 1978 (12.6 to 23.2 ppb) and leveled off during the winter and spring months (2.9 to 5.6 ppb). Increases in colloidal copper were observed during the late spring and summer months (2.3 to 6.4 ppb).

COPPER IN PARTICULATE MATERIAL

The levels of copper present in particulate material at the PIER, INLET, and NAVY sites are presented in figure 5. The individual values are also given in appendix table 3.

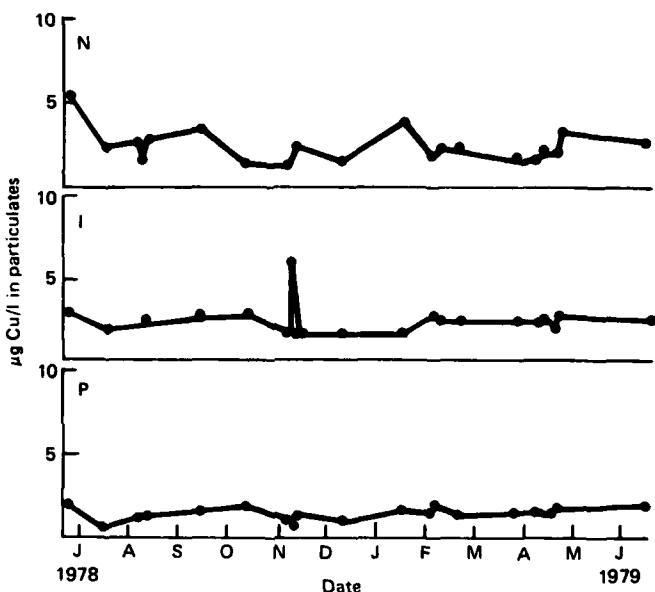


Figure 5. Levels of copper associated with particulate material in terms of micrograms Cu/l at the PIER (P), INLET (I), and NAVY (N) sites from July 1978 through June 1979.

The level of copper in particulate material at the PIER site was fairly uniform over the year at a concentration of 1.8 $\mu\text{g/l}$. A low level of 0.7 $\mu\text{g/l}$ occurred during August 1978.

The levels of copper in particulate material at the INLET site also were fairly uniform over the year. Low levels of 1.5 $\mu\text{g/l}$ occurred during the winter months. Levels fluctuated around 2.4 $\mu\text{g/l}$ during the remainder of the year. An extremely high concentration of 5.6 $\mu\text{g/l}$ was encountered during late November 1978. There is a possibility that this sample was contaminated during some stage of the filtration procedure.

The level of copper in the particulate material at the NAVY site varied much more than did levels at the PIER and INLET sites. Levels decreased irregularly from August 1978 (5.2 $\mu\text{g/l}$) through late December 1978 (1.5 $\mu\text{g/l}$). A sharp increase in particulate copper was observed in February 1979 (3.9 $\mu\text{g/l}$) but leveled off during the spring (2.1 $\mu\text{g/l}$). Particulate copper increased again during the early summer (3.3 $\mu\text{g/l}$).

Results of the Friedman test, followed by the nonparametric multiple range test, indicate that the PIER site maintained significantly lower levels of copper associated with particulate material than did either the INLET or NAVY sites (p values < 0.05). There were no other significant differences (p values > 0.05).

PRIMARY PRODUCTIVITY

To determine the rate of primary productivity of the phytoplankton, ^{14}C uptake studies were performed. These rates of primary productivity, expressed in terms of $\mu\text{g C uptake/l/h}$, are shown in figure 6. The individual values are also given in appendix table 4.

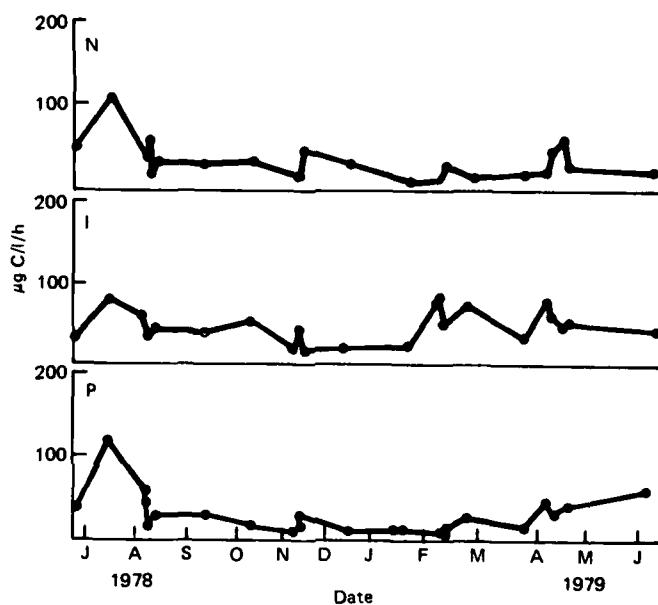


Figure 6. Primary productivity ($\mu\text{g C uptake/l/h}$) of the phytoplankton assemblages taken from the PIER (P), INLET (I), and NAVY (N) sites from July 1978 through June 1979.

The data summarized in figure 6 indicate that trends in primary productivity were similar for the three sites. Levels were highest during late summer (111.15 $\mu\text{g C/l/h}$ at the PIER site, 74.95 $\mu\text{g C/l/h}$ at the INLET site, and 106.0 $\mu\text{g C/l/h}$ at the NAVY site) and spring (44.12, 72.62, and 52.56 $\mu\text{g C/l/h}$ at the PIER, INLET, and NAVY sites, respectively). Low levels of productivity occurred during the late fall and winter months (5.17, 13.26, and 3.40 $\mu\text{g C/l/h}$ at the PIER, INLET, and NAVY sites, respectively). The results of a Friedman test, followed by the nonparametric multiple range test, indicate that the phytoplankton from the INLET site maintain significantly higher rates of productivity than those taken from either the PIER or NAVY sites (p values < 0.05). There were no other significant differences (p values > 0.05).

CHLOROPHYLL A

The levels of chlorophyll A in mg/m^3 at the three sites over the year are shown in figure 7. The individual values are also given in appendix table 4. Figure 7 indicates that the trend in chlorophyll A concentration was similar at all three sites. As with productivity, levels of chlorophyll A are highest during late summer and spring, and decrease during the fall and winter months.

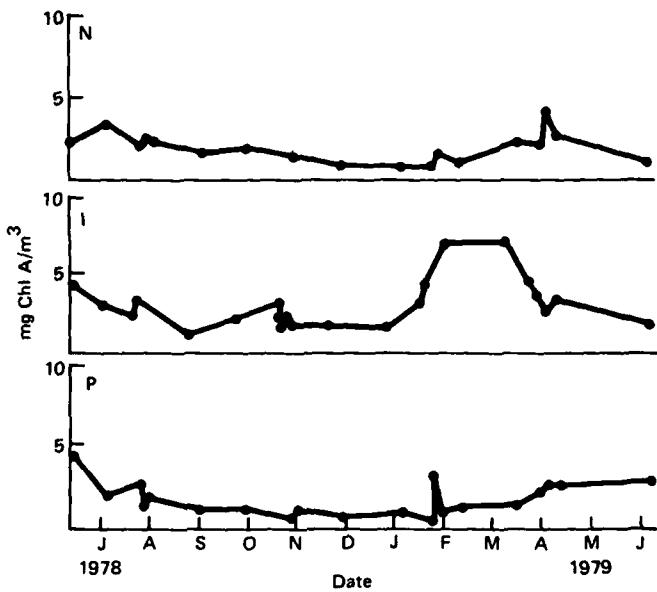


Figure 7. Chlorophyll A levels (mg/m^3) of the phytoplankton assemblages taken from the PIER (P), INLET (I), and NAVY (N) sites from July 1978 through June 1979.

Chlorophyll A decreased from August levels of 4.46 mg/m^3 at the PIER site, 4.45 mg/m^3 at the INLET site, and 3.11 mg/m^3 at the NAVY site, to winter levels of 0.77 , 1.77 , and 0.63 mg/m^3 at the PIER, INLET, and NAVY sites, respectively. Chlorophyll A levels increased from these low concentrations over the spring months to concentrations of 2.76 , 6.75 , and 3.79 mg/m^3 at the PIER, INLET, and NAVY sites, respectively.

Friedman analysis followed by nonparametric multiple comparisons indicates that the INLET site maintained a significantly higher phytoplankton biomass than either the PIER or NAVY sites (p values < 0.05). There were no other significant differences (p values > 0.05).

PRODUCTIVITY INDEX

As a means of comparing different phytoplankton assemblages from different areas, productivity indices were calculated. The productivity indices for the three sites over the year are shown in figure 8. The individual values are also listed in appendix table 4.

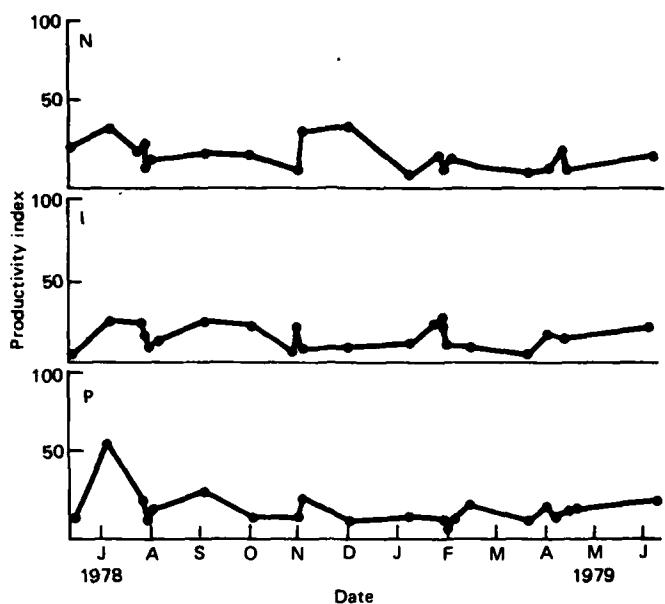


Figure 8. Trends in productivity indices of the phytoplankton assemblages taken from the PIER (P), INLET (I), and NAVY (N) sites. Productivity index is given as productivity/biomass. Samples were collected from July 1978 through June 1979.

These indices did not fluctuate significantly from a value of 15.0 over the year. However, an exception occurred during August 1978, at which time the productivity index for all three sites increased to values of 54.4, 25.6, and 34.1 for the PIER, INLET, and NAVY sites, respectively. The results of a Friedman test on these data indicate that there were no significant differences among productivity indices for the three phytoplankton assemblages ($p > 0.05$).

PHYTOPLANKTON COMPOSITION AND DIVERSITY

The genera of phytoplankton taken at the three field sites are given in table 1. Appendix table 5 lists both the genera of phytoplankton and the estimated number of cells per liter at the three sites. The major genera of diatoms encountered during the study were *Chaetoceros*, *Asterionella*, *Leptocylindrus*, *Nitzschia*, *Skeletonema* and an unidentified diatom I designated as Diatom #12. This unidentified alga is a pennate, chain-forming diatom with cells 2 μm in diameter by 15 μm in length. Chains of two to 50 cells in length were encountered. The major genera of dinoflagellates encountered were *Gonyaulax*, *Peridinium* and *Prorocentrum*. An unidentified biflagellate was encountered at all three sites in moderate densities. This form, referred to as Genus #5, was more frequently encountered at the INLET site than at the other two sites. Although complete identification of this form was not possible, it is thought to be of the genus *Dunaliella*.

The percentage compositions of the six most frequently encountered diatoms at the three sites over the year are given in figures 9 - 14. These percentages were calculated as the

Genus	PIER	INLET	NAVY
<i>Ceratium</i>	X	X	X
<i>Gymnodinium</i>	X	--	X
<i>Dinophysis</i>	X	--	X
<i>Gonyaulax</i>	X	X	X
<i>Noctulica</i>	X	--	-
<i>Peridinium</i>	X	X	X
<i>Prorocentrum</i>	X	X	X
<i>Asterionella</i>	X	X	X
<i>Bidulphia</i>	X	--	X
<i>Ceratulina</i>	X	X	X
<i>Chaetoceros</i>	X	X	X
<i>Coscinodiscus</i>	X	X	X
<i>Ditylum</i>	X	X	X
<i>Eucampia</i>	X	X	X
<i>Leptocylindrus</i>	X	X	X
<i>Licomorpha</i>	X		
<i>Navicula</i>	X	X	X
<i>Nitzschia</i>	X	X	X
<i>Rhizosolenia</i>	X	X	X
<i>Skeletonema</i>	X	X	X
<i>Thalassiosira</i>	X	X	X
<i>Thalassiothrix</i>	X	X	X
<i>Achnanthes</i>	X	--	-
<i>Streptotheca</i>	X	--	X
<i>Thalassionema</i>	X	--	-
<i>Pleurosigma</i>	X	--	--
<i>Diatom #12</i>	X	X	X
<i>Stephanophysix</i>	X	--	--
<i>Diatom #19</i>	--	X	X
<i>Suriella</i>	X	X	X
<i>Genus #5</i>	X	X	X

Table 1. Genera of phytoplankton taken at the PIER, INLET, and NAVY sites from July 1978 through June 1979.

number of cells of a given genus versus the total number of all phytoplankton cells present in a given sample. The data shown in figure 9 indicate that the unidentified Diatom #12 was the predominant form in early fall at all three sites. It comprised 75, 92, and 60% of the assemblages at the PIER, INLET, and NAVY sites, respectively, during this time.

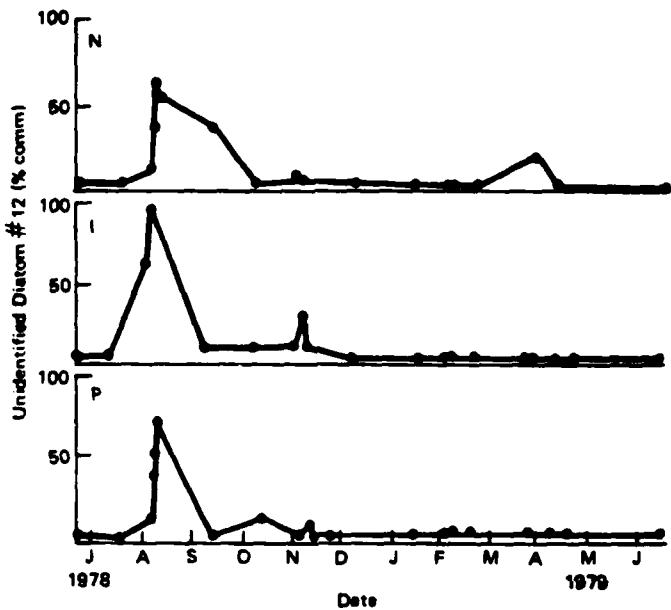


Figure 9. Percent community composition of the Unidentified Diatom #12 from July 1978 through June 1979 at the PIER (P), INLET (I), and NAVY (N) sites.

Leptocylindrus was also frequently encountered during the fall. This diatom comprised 55% of all phytoplankton cells at both the PIER and NAVY sites (figure 10). However, *Leptocylindrus* was rarely encountered at the INLET site.

Chaetoceros was the major form encountered during the winter (figure 11). At the NAVY and PIER sites, it formed nearly 99% of the total phytoplankton cells, and at the INLET site, 80%. *Chaetoceros* was also encountered at the PIER and INLET sites during the spring, but at lower densities than during the winter.

Asterionella was the numerically dominant form during February and March 1979 at all three sites (figure 12). This diatom represented more than 90% of the total phytoplankton cells present at the times of sampling.

Skeletonema occurred throughout the entire year at all three field sites (figure 13). *Skeletonema* formed less than 50% of the total phytoplankton cells at the PIER and NAVY sites and formed up to 70% at the INLET site during the period of peak densities.

Nitzschia formed 95, 45, and 98% of the phytoplankton cells at the PIER, INLET, and NAVY sites, respectively, during the spring (figure 14). *Nitzschia* was also encountered at much lower densities during the fall at all three field sites.

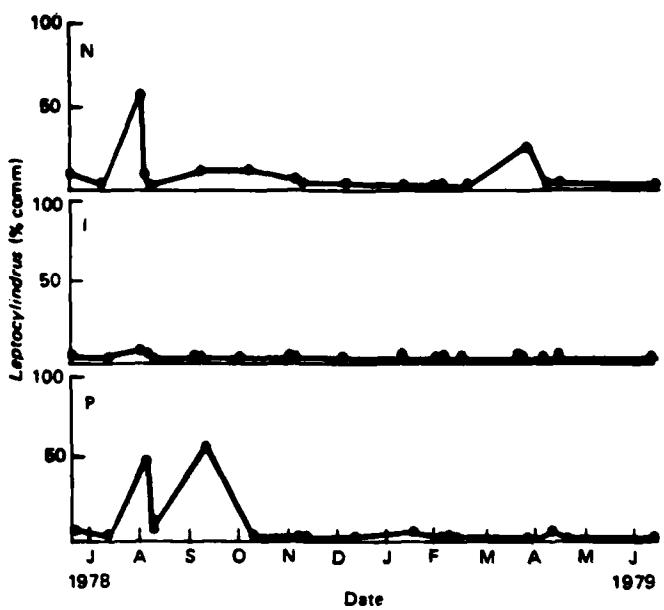


Figure 10. Percent community composition of *Leptocylindrus* from July 1978 through June 1979 at the PIER (P), INLET (I), and NAVY (N) sites.

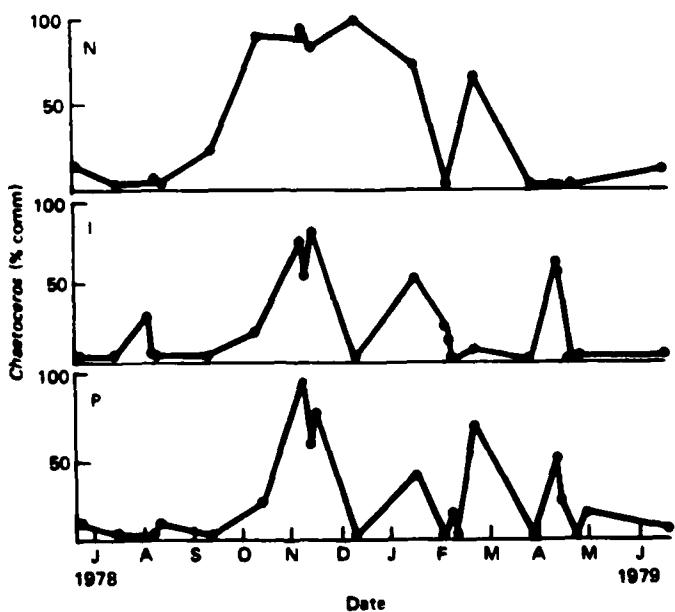


Figure 11. Percent community composition of *Chaetoceros* from July 1978 through June 1979 at the PIER (P), INLET (I), and NAVY (N) sites.

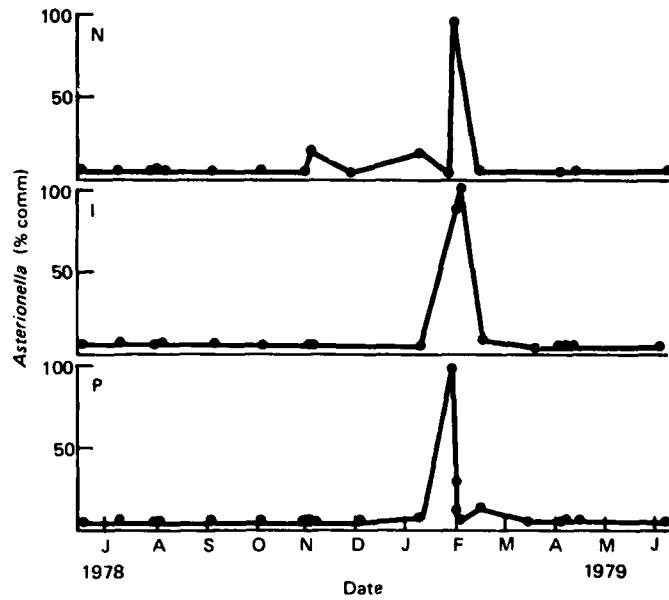


Figure 12. Percent community composition of *Asterionella* from July 1978 through June 1979 at the PIER (P), INLET (I), and NAVY (N) sites.

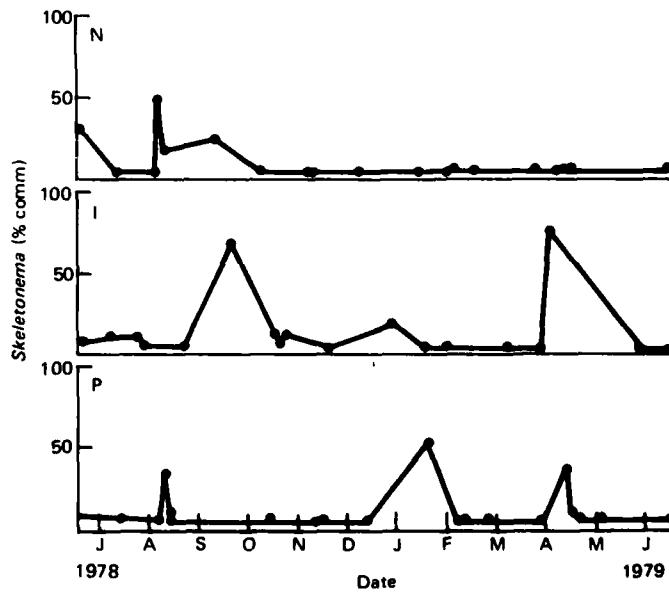


Figure 13. Percent community composition of *Skeletonema* from July 1978 through June 1979 at the PIER (P), INLET (I), and NAVY (N) sites.

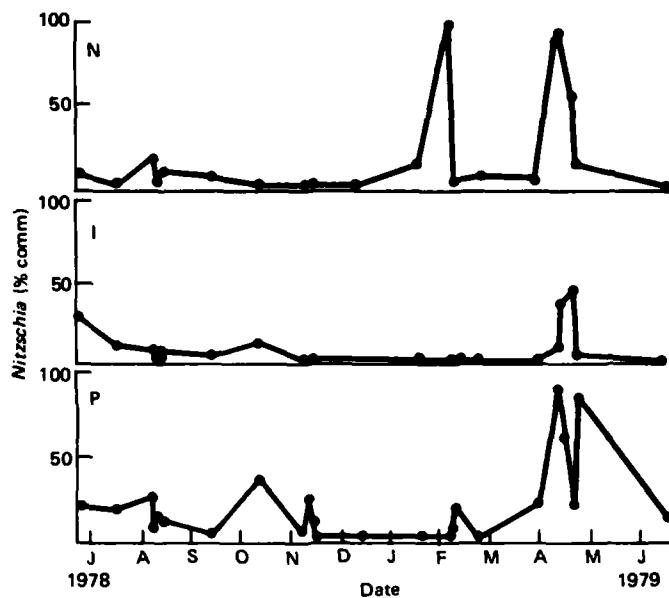


Figure 14. Percent community composition of *Nitzschia* from July 1978 through June 1979 at the PIER (P), INLET (I), and NAVY (N) sites.

Diversity indices were calculated, based on the number of genera encountered and the density of individuals per genus. These indices are shown in figure 15 and the individual

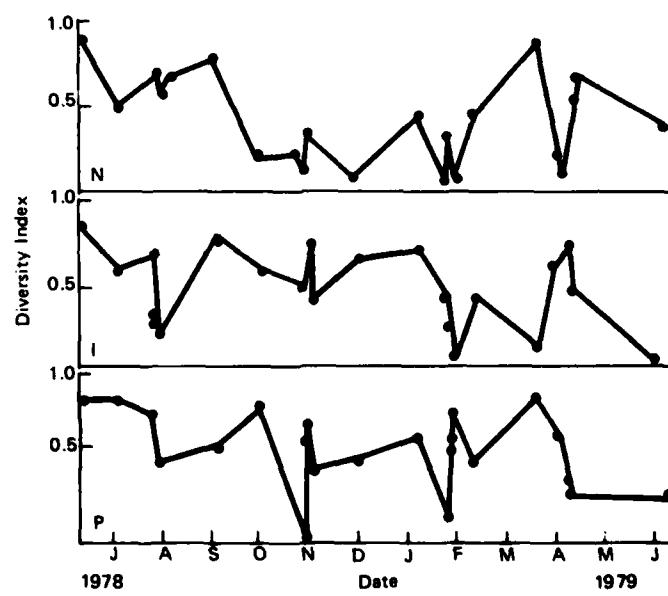


Figure 15. Trends in the diversity indices of phytoplankton communities taken from the PIER (P), INLET (I), and NAVY (N) sites from July 1978 through June 1979.

values are listed in appendix table 4. The data in figure 15 indicate a highly irregular pattern in the trends of diversity over the year at all three sites. However, the results of a Friedman test on these data indicate no significant difference in diversity indices among the three sites ($p > 0.05$).

Indices of diversity were highest at the PIER and NAVY sites during the late summer and spring. Low diversity indices were generally encountered during the winter and early summer for both the PIER and NAVY sites. These trends followed patterns of light availability and temperature conditions. The reverse trend, however, was encountered at the INLET site. Diversity indices decreased over the summer and fall months, were elevated during the winter, and depressed during the spring.

TOXICITY EXPERIMENT

Productivity of the phytoplankton assemblage from the PIER site ($\mu\text{g C uptake/l/h}$) as a function of added copper exhibited decreasing trends with increasing levels of copper (figure 16). Levels of productivity decreased from 23.9 $\mu\text{g C/l/h}$ at 2.7 ppb soluble copper to 4.7 $\mu\text{g C/l/h}$ at 13.4 ppb soluble copper. Productivity continued to decrease to 2.04 $\mu\text{g C/l/h}$ as copper increased to 47.1 ppb.

The INLET assemblage also exhibited decreasing productivity with increasing levels of copper, but at a slower rate than encountered with the PIER assemblage (figure 16). Productivity increased initially with increasing levels of copper to 14.0 $\mu\text{g C/l/h}$ at 9.8 ppb soluble copper. From this point on productivity decreased to a level of 7.2 $\mu\text{g C/l/h}$ at 14.8 ppb soluble copper and 6.8 $\mu\text{g C/l/h}$ at 40.4 ppb soluble copper.

Chlorophyll A trends as a function of copper level are presented in figure 17. These data indicate a decreasing level of chlorophyll A with increasing copper concentration for phytoplankton assemblages at both the PIER and INLET sites. However, the rate of decrease in chlorophyll A was less for the INLET assemblage. Chlorophyll A levels decreased from 1.8 to 0.88 mg/m³ for the PIER assemblage, with levels of soluble copper increasing from 1.3 to 47.1 ppb. Chlorophyll A levels decreased from 2.72 to 2.26 mg/m³ for the INLET assemblage, with levels of soluble copper increasing from 2.1 to 40.4 ppb.

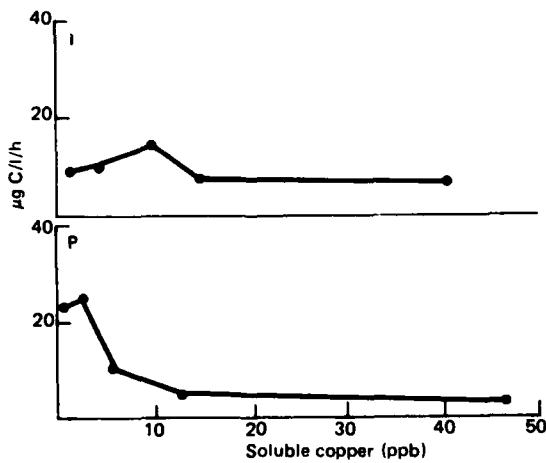


Figure 16. Primary production ($\mu\text{g C/l/h}$) of the PIER (P) and INLET (I) assemblages as a function of added copper (ppb).

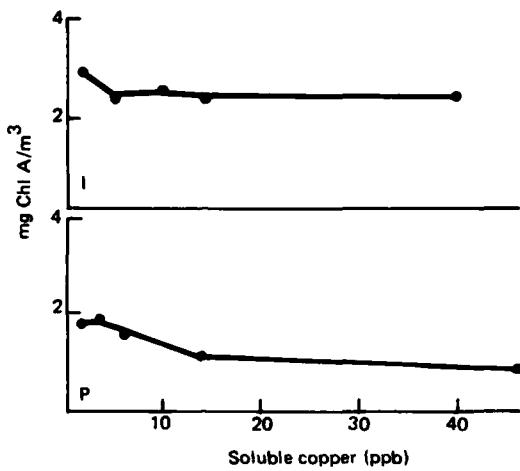


Figure 17. Trends in Chlorophyll A levels (mg/m^3) of the PIER (P) and INLET (I) assemblages as a function of added copper (ppb).

The trends in productivity index (figure 18) coincide well with the trends in productivity. The productivity index decreased with increasing levels of soluble copper at the PIER site. The productivity index increased initially with increasing soluble copper at the INLET site, then decreased with the higher levels of soluble copper. Initially, the productivity index determined for the PIER assemblage was greater than that determined for the INLET assemblage (13.3 for the PIER as compared to 3.47 for the INLET). However, as soluble

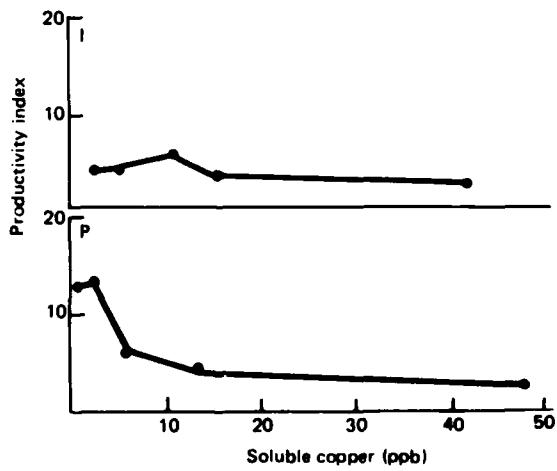


Figure 18. Trends in the productivity indices of the PIER (P) and INLET (I) assemblages as a function of added copper (ppb).

copper levels increased to approximately 50 ppb, the productivity index for the PIER assemblage decreased to 2.45 and the productivity index for the INLET assemblage decreased to 2.96. The individual values for productivity, chlorophyll A, productivity indices, and for copper present in the soluble, colloidal, and total fractions of seawater are presented in appendix tables 6 and 7.

The genera and density of phytoplankton (number of individuals per genus) encountered at the various concentrations for each study site are presented in tables 2 and 3. At low copper levels, the PIER assemblage maintained more genera than did the INLET assemblage. Both assemblages showed a decrease in the number of genera encountered with increasing levels of soluble copper. In terms of density, the dominant genus present in the PIER assemblage was *Nitzschia*. The dominant genus of the INLET assemblage was Genus #5.

RESULTS OF STATISTICAL ANALYSES

Multiple Partial Correlation Analysis

Multiple partial correlation analysis performed on all variables showed significant positive correlations (p values < 0.05) between productivity/Chlorophyll A, productivity index/productivity, and productivity index/Chlorophyll A for the PIER and NAVY sites, while there were significant positive correlations between productivity/productivity index for the INLET site (table 4). These results indicate that there was a strong correlation between rate of productivity and phytoplankton biomass.

As indicated in table 5, the second multiple partial correlation analysis performed on only the phytoplankton characteristics, copper data, and nutrient levels showed no significant correlations (p values > 0.05). These results suggest that growth and diversity of phytoplankton were not correlated with copper levels.

Genus	Copper Level				
	Ambient	Ambient +5 ppb	Ambient +10 ppb	Ambient +20 ppb	Ambient +50 ppb
<i>Ceratium</i>	0	4	4	0	0
<i>Dinophysis</i>	0	4	0	0	0
<i>Gonyaulax</i>	8	28	8	0	0
<i>Peridinium</i>	16	0	12	0	0
<i>Prorocentrum</i>	0	0	4	0	0
<i>Asterionella</i>	0	0	8	0	12
<i>Biddulphia</i>	4	4	0	0	0
<i>Ceratulina</i>	0	12	0	0	0
<i>Chaetoceros</i>	84	80	16	0	0
<i>Coscinodiscus</i>	12	8	16	0	0
<i>Ditylum</i>	0	0	4	0	0
<i>Navicula</i>	8	0	8	4	8
<i>Nitzschia</i>	260	444	420	196	152
<i>Rhizosolenia</i>	4	8	8	0	0
<i>Skeletonema</i>	8	12	0	0	0
Genus #5	16	36	36	68	16
Diatom #12	0	0	32	0	0

Table 2. The genera and density (number of cells $\times 10^2$ /liter) of phytoplankton taken from the PIER site under conditions of elevated copper levels (ppb).

Genus	Copper Level				
	Ambient	Ambient +5 ppb	Ambient +10 ppb	Ambient +20 ppb	Ambient +50 ppb
<i>Ceratium</i>	4	4	8	0	0
<i>Gonyaulax</i>	24	4	0	0	0
<i>Peridinium</i>	16	0	0	0	0
<i>Prorocentrum</i>	4	0	0	0	0
<i>Chaetoceros</i>	0	0	0	12	0
<i>Nitzschia</i>	8	0	0	12	8
<i>Skeletonema</i>	0	0	0	16	0
Genus #5	952	1368	1112	1172	620

Table 3. The genera and density (number of cells $\times 10^2$ /liter) of phytoplankton taken from the INLET site under conditions of elevated copper levels (ppb).

Friedman Test

To determine whether differences existed in the phytoplankton characteristics and copper levels among the three sites, nonparametric Friedman tests were performed on the data. The results of these tests are presented in table 6.

The results of these tests indicate that the INLET site had significantly higher phytoplankton biomass and levels of productivity than did the other two sites (p values < 0.05). There were no other significant differences in productivity indices or diversity (p values > 0.05). These results suggest that the phytoplankton communities in high copper and low copper regions were similar in these characteristics. The three sites apparently have the potential of maintaining phytoplankton assemblages of similar composition.

The results of Friedman analysis and nonparametric multiple range tests performed on the copper data indicate that the PIER site had significantly lower levels of copper both in the soluble fraction and associated with particulate material than either the INLET or NAVY sites (p values < 0.05). The total copper levels and the copper levels associated with colloidal material were significantly different at each site (p values < 0.05).

Variable	PIER									
	Pro	Cnl	Pl	Temp	Salt	Tide	pH	Part	Solb	Total
Productivity	1.000	0.828	0.845	-0.462	0.442	-0.323	-0.077	0.052	0.073	0.347
Chlorophyll A		1.000	-0.786	0.515	-0.301	0.062	0.241	0.191	-0.010	0.150
Productivity index			1.000	0.416	-0.216	0.129	0.114	-0.093	0.081	-0.168
Temperature				1.000	0.422	-0.010	-0.037	0.046	0.261	0.122
Salinity					1.000	0.324	0.095	-0.452	-0.187	-0.219
Tidal stage						1.000	0.150	0.408	0.398	-0.112
pH							1.000	-0.257	-0.279	0.285
Particulate Cu								1.000	-0.244	-0.119
Soluble Cu									1.000	-0.397
Total copper										0.045
Colloidal Cu										1.000
Particulate	Sum									
	Diversity									
Productivity	0.152	0.212								
Chlorophyll A	0.067	0.025	0.120							
Productivity index	-0.097	-0.175	0.362							
Temperature	0.340	0.146	0.105							
Salinity	-0.219	-0.084	0.165							
Tidal stage	0.319	0.298	-0.026							
pH	-0.471	-0.059	-0.063							
Particulate Cu	0.454	-0.382	0.551							
Soluble Cu	-0.452	-0.205	-0.092							
Total copper	-0.260	-0.458	0.176							
Colloidal Cu	-0.029	-0.242	0.428							
Particulates	1.000	-0.260	0.080							
Diversity		1.000	0.184							
Soluble Cu +			1.000							
Particulate Cu				1.000						

Table 4. Correlation coefficients produced by the multiple partial correlation analysis performed on 14 variables. At the 95% confidence level and n = 11 degrees of freedom, significant coefficients are ≥ 0.553 .

Table 4. (Continued).

Variable	NAVY						Coll		
	Pro	Chl	PI	Temp	Salt	Tide	Part	Solb	Total
Productivity	1.000	0.874	0.877	0.097	-0.228	0.272	0.081	0.391	-0.514
Chlorophyll A		1.000	-0.771	0.093	0.140	-0.252	0.088	-0.414	0.541
Productivity index			1.000	-0.104	0.399	-0.427	0.090	-0.362	-0.546
Temperature				1.000	0.193	-0.283	0.369	0.086	-0.263
Salinity					1.000	0.642	-0.103	0.116	-0.384
Tidal stage						1.000	0.351	-0.122	-0.514
pH							1.000	0.052	0.281
Particulate Cu								1.000	-0.324
Soluble Cu									0.360
Total Cu									0.325
Colloidal Cu									-0.445
	Diversity						Sum		
Productivity		-0.365		0.002			-0.405		
Chlorophyll A		0.327		0.055			0.371		
Productivity index		0.307		-0.155			0.480		
Temperature		0.193		0.116			0.177		
Salinity		-0.305		0.291			-0.410		
Tidal stage		0.365		-0.290			0.512		
pH		-0.083		-0.088			-0.162		
Particulate		0.348		-0.057			0.775		
Soluble Cu		-0.336		0.155			-0.644		
Colloidal Cu		0.593		0.059			0.526		
Particulates		1.000		-0.117			-0.470		
Diversity				1.000			0.328		
Soluble Cu +							1.000		
Particulate Cu							-0.191		

Table 4. (Continued)

Variable	PIER						INLET					
	Pro	Chl	PI	Dvtr	Solb	Diff	Total	Coll	Part	PO ₄	SiO ₄	
Productivity	1.000	0.864	0.919	0.131	0.448	0.523	-0.492	-0.068	-0.544	-0.029	-0.464	
Chlorophyll A		1.000	-0.854	-0.036	-0.481	-0.549	0.528	0.254	0.659	-0.167	0.579	
Productivity index			1.000	-0.101	-0.446	-0.545	0.521	0.122	0.503	0.002	0.571	
Diversity				1.000	-0.010	-0.020	-0.026	-0.068	-0.170	-0.216	0.154	
Soluble Cu					1.000	-0.971	0.972	0.317	0.303	0.433	0.354	
Total Cu - Soluble Cu						1.000	0.993	0.266	0.356	0.424	0.475	
Total Cu							1.000	-0.240	-0.379	-0.440	-0.461	
Colloidal Cu								1.000	-0.059	0.143	0.095	
Particulate Cu									1.000	0.065	-0.407	
Phosphates										1.000	-0.030	
Silicates											1.000	

Table 5. Correlation coefficients produced by the multiple partial correlation analysis performed on phytoplankton characteristics, copper, and nutrients. At the 95% confidence level and n = 8 degrees of freedom, significant coefficients are ≥ 0.632 .

Variable	NAVY							
	<u>Pro</u>	<u>Chl</u>	<u>PI</u>	<u>Divr</u>	<u>Solb</u>	<u>Diff</u>	<u>Total</u>	<u>Coll</u>
Productivity	1.000	0.514	0.885	-0.468	-0.267	-0.095	0.220	-0.029
Chlorophyll A		1.000	-0.372	-0.073	-0.499	-0.534	0.496	0.360
Productivity index			1.000	0.585	0.265	0.020	-0.159	0.011
Diversity				1.000	-0.375	-0.158	0.269	0.101
Soluble Cu					1.000	-0.890	0.946	0.397
Total Cu - Soluble Cu						1.000	0.968	0.318
Total Cu							1.000	-0.229
Colloidal Cu								1.000
Particulate Cu								1.000
Phosphates								0.066
Silicates								0.801
								1.000

Table 5. (Continued).

<u>Variable</u>	χ^2_{Calc}	<u>Multiple Comparison</u>		q_{crit}
			q_{calc}	
Productivity	6.84	P vs I	3.54	3.31
		N vs I	2.71	2.77
		N vs P	0.83	2.77
Chlorophyll A	12.72	P vs I	4.38	3.54
		N vs I	4.38	2.77
		N vs P	0.00	2.77
Productivity index	0			
Diversity index	3.21			
Soluble copper	34.68	P vs I	7.51	3.31
		N vs I	0.62	2.77
		N vs P	6.88	2.77
Total copper	48.24	P vs I	8.76	3.31
		N vs I	2.71	2.77
		N vs P	6.05	2.77
Colloidal copper	31.39	P vs I	7.93	3.31
		N vs I	3.93	2.77
		N vs P	3.96	2.77
Particulate copper	18.35	P vs I	5.74	3.31
		N vs I	1.56	2.77
		N vs P	4.27	2.77

Table 6. Results of the Friedman randomized block analysis of variance by ranks. N = 23 for data from the PIER, INLET and NAVY sites. $\chi^2_{\text{crit}} = 5.991$.

TEMPERATURE

The temperature of seawater determined at the time of sample collection followed cyclic sinusoidal patterns at all three sites (figure 19). The temperatures decreased during the fall and winter months to a low of 13.0, 12.0, and 13.2°C at the PIER, INLET, and NAVY sites, respectively. The temperature rose during January through May to 17.0, 18.0, and 19.0°C at the PIER, INLET, and NAVY sites, respectively. Summer temperatures were between 18.8 and 21.0°C at the PIER site, 19.5 and 22.0°C at the INLET site, and 19.0 and 24.5°C at the NAVY site. Yearly mean temperatures at the PIER, INLET, and NAVY sites are 16.9, 17.2, and 18.7°C, respectively. The individual values measured during the year for the three sites are given in appendix table 8.

The values obtained at the NAVY site were slightly higher than those of the PIER and INLET sites because this location is near the inner end of the bay in a shallow area with

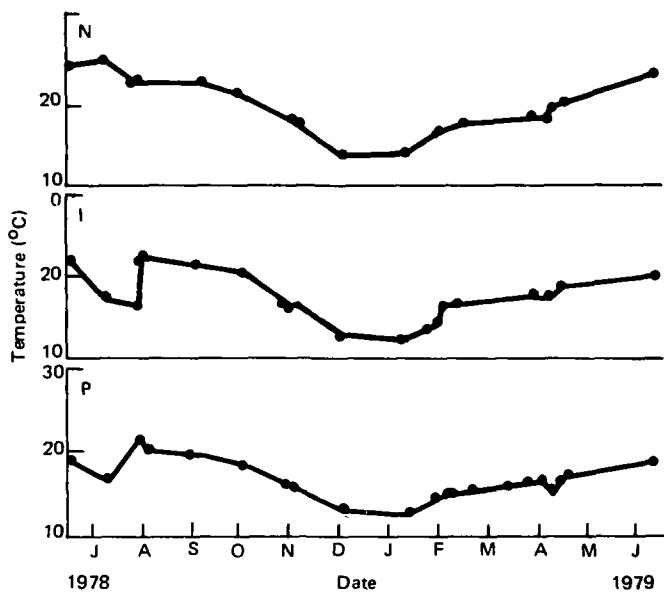


Figure 19. Trends in temperature ($^{\circ}\text{C}$) at the PIER (P), INLET (I), and NAVY (N) sites from July 1978 through June 1979.

poor tidal circulation. The temperature measurements for the PIER site followed open-ocean temperatures because this site is very close to the entrance of the channel to San Diego Bay.

The temperature values obtained in this study are what would be expected for a body of water such as San Diego Bay at this latitude (San Diego Gas and Electric Company, 1973a, 1973b, 1973c). The range in temperature values was similar for the three sites. These results suggest that variations in phytoplankton characteristics observed among the three sites probably were not the result of temperature.

SALINITY

The salinity values obtained at the three sites are shown in figure 20. High salinity levels of 36.0, 36.5, and 37.0 ppt were reached for the PIER, INLET, and NAVY sites, respectively, during August 1978. Low salinity levels of 30.7, 29.3, and 22.2 ppt were reached for the PIER, INLET, and NAVY sites, respectively, during January 1979. The mean salinity values were 33.0, 32.9, and 32.6 ppt for the PIER, INLET, and NAVY sites, respectively. Figure 20 indicates that, other than during August and January, the salinity levels characteristic of these sites showed very little fluctuation around these means. The individual values are presented in appendix table 8.

High salinities during August were the result of evaporation as the result of elevated temperatures or stratification in the water column. The low salinities encountered during January and February were the result of dilution from runoff and rain. During this 2-month period, San Diego experienced several weeks of heavy rains.

The range of salinities measured at the three sites over the year is very narrow. Salinity was probably not responsible for observed variations in phytoplankton characteristics at the three sites.

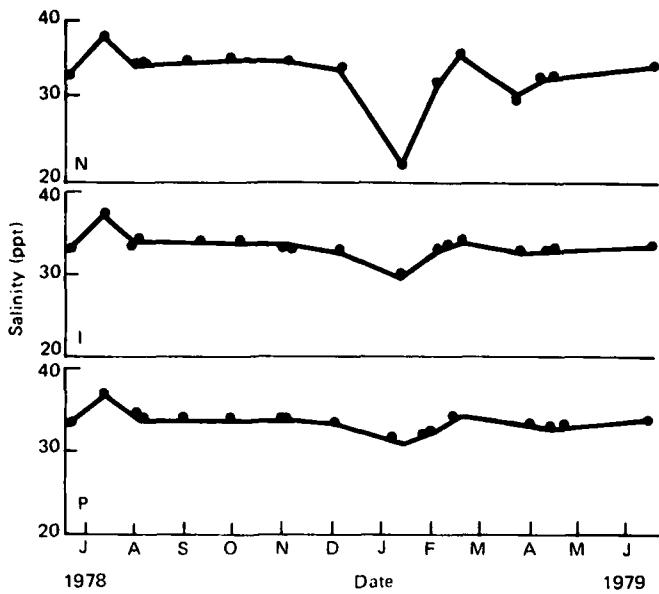


Figure 20. Trends in salinity (ppt) at the PIER (P), INLET (I), and NAVY (N) sites from July 1978 through June 1979.

pH

The pH values of the seawater at the PIER, INLET, and NAVY sites determined over the 1-year period are shown in figure 21. The trends in pH are similar at all three sites. The

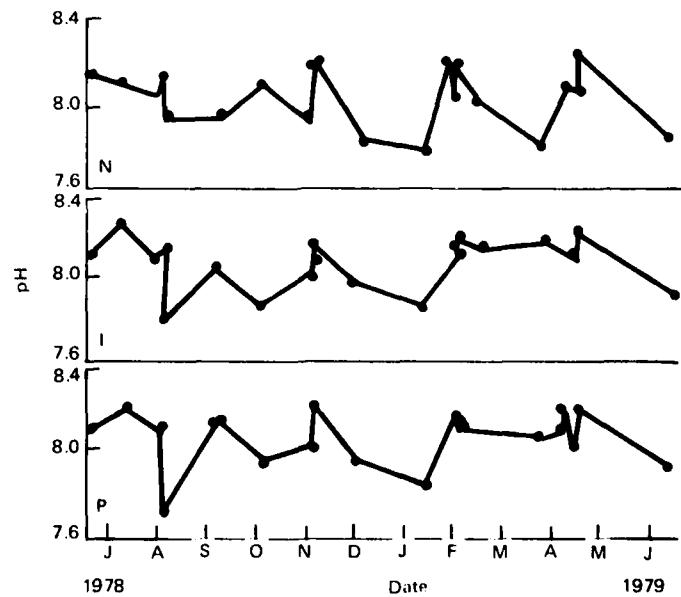


Figure 21. Trends in pH at the PIER (P), INLET (I), and NAVY (N) sites from July 1978 through June 1979.

curves in figure 21 suggest that there is a great deal of variability in the pH of seawater in San Diego Bay. The mean of the pH measurements was 8.1 for all three sites.

Major decreases in pH were observed during August 1978 and January and February 1979. A complete listing of the pH measurements is given in appendix table 8.

The fluctuations observed in pH measurements over the year were probably the result of photosynthetic activities. Such fluctuations in pH are characteristic of bay environments (Zirino, personal communication).

TIDAL STAGE

The stage of the tidal cycle, whether incoming, outgoing, or between tides, was noted at the time the samples were collected. The position was coded with 1 = incoming tide, 2 = outgoing tide, 0 = changing tide. These individual data for the three sites over the year are given in appendix table 8.

The stage of the tidal cycle is important in considering both copper concentrations and phytoplankton characteristics. An outgoing tide may bring copper-contaminated water past the sample site, while incoming tides may "dilute" the sample water. High variations in phytoplankton diversity may be observed during changing tidal cycles. During the year, the tidal stage was generally the same for all three sites at the time of sample collection. Therefore, observed variations in copper measurements or phytoplankton characteristics presumably were not the result of tidal stage.

NUTRIENTS

Nitrite

Nitrite concentration (figure 22) exhibited widely fluctuating patterns at the three sample sites. Relatively high concentrations of 0.5, 0.64, and 1.34 $\mu\text{g-at/l}$ for the PIER,

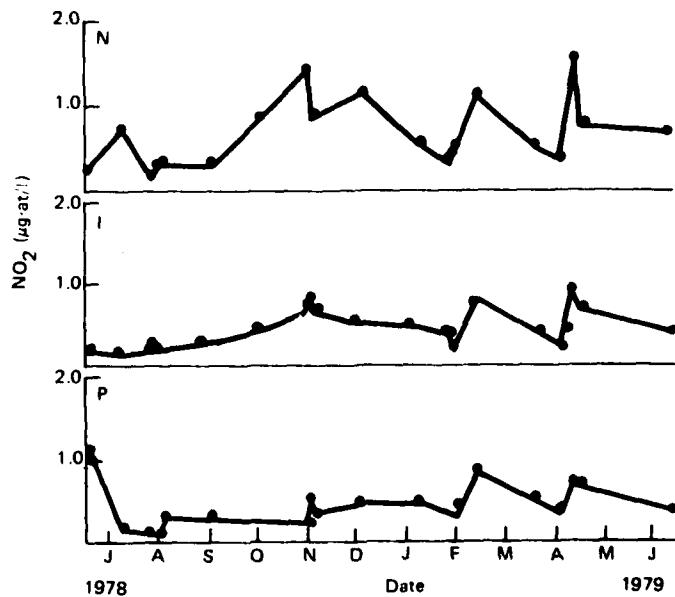


Figure 22. Trends in nitrite concentration ($\mu\text{g-at NO}_2/\ell$) at the PIER (P), INLET (I), and NAVY (N) sites from July 1978 through June 1979.

INLET, and NAVY sites, respectively, occurred during late November 1978. These levels decreased through early February. Peak levels are again reached during late February and early March 1979 (0.5, 0.52, and 0.54 $\mu\text{g-at/l}$ for the PIER, INLET, and NAVY sites, respectively). A third peak in nitrite availability occurred during early May with levels reaching 0.79, 0.87, and 1.42 $\mu\text{g-at/l}$ at the PIER, INLET, and NAVY sites, respectively. Low levels of nitrite occurred during early winter and late spring. Concentrations range between 0.06 and 0.14 $\mu\text{g-at/l}$ during this time.

The data in figure 22 also indicate that nitrite levels are greater at the INLET and NAVY sites over the year than at the PIER site.

Several of the nitrite and nitrate values indicated contamination of the sample, with the levels exceeding 1000 $\mu\text{g-at/l}$. This contamination was determined to be the result of inadequate rinsing of the sample bottles after acid washing. Nitrates and nitrites were excluded from the correlation analysis for this reason.

Nitrate

Nitrate concentration (figure 23) varied significantly at the PIER, INLET, and NAVY sites in San Diego Bay during the year. However, concentration ranges are similar for all three sites. The complete set of values for nitrate levels is given in appendix table 9.

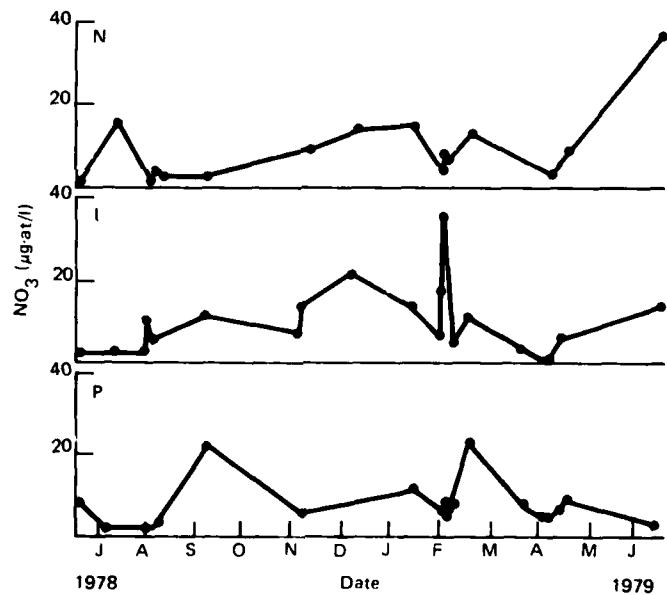


Figure 23. Trends in nitrate concentrations ($\mu\text{g-at NO}_3/\ell$) at the PIER (P), INLET (I), and NAVY (N) sites from July 1978 through June 1979.

The PIER site was characterized by the occurrence of peak nitrate availability during February and March 1979. These levels were 21.4 and 22.4 $\mu\text{g-at/l}$, respectively. During the remainder of the year, nitrate concentrations varied around a mean of approximately 6.6 $\mu\text{g-at/l}$. Extreme low concentrations were observed during late fall (0.60 to 0.51 $\mu\text{g-at/l}$).

The INLET site was characterized by the occurrence of peak nitrate concentrations during February 1979. Concentrations increased from a level of 0.50 $\mu\text{g-at/l}$ during the fall (late August 1978) to 20.6 $\mu\text{g-at/l}$ during February, 1979, after which nitrate concentrations stabilized at approximately 6.0 $\mu\text{g-at/l}$.

The NAVY site was characterized by nitrate concentrations ranging between 0.81 and 14.70 $\mu\text{g-at/l}$. A peak concentration of 15.4 $\mu\text{g-at/l}$ was observed during August 1978. This concentration apparently was rapidly depleted to 0.8 $\mu\text{g-at/l}$ by September 1978. Concentrations gradually increased over the winter and spring months to a peak concentration of 14.7 $\mu\text{g-at/l}$ observed during February 1979. The nitrate concentration decreased during the spring and early summer to a low level of 2.5 $\mu\text{g-at/l}$ in May 1979. A high concentration of nitrate was detected during June 1979. However, it is believed that this may have resulted from contamination of the sample by slight traces of nitric acid.

Nitrate concentrations at all three sites were generally well above the limiting level of 1.0 $\mu\text{g-at/l}$ (Thomas, 1966). This suggests that nitrate, an important nutrient for phytoplankton growth, remained at nonlimiting concentrations in San Diego Bay during the year.

Phosphate

Phosphate levels for the PIER, INLET, and NAVY sites are shown in figure 24. The trends are similar for all three sites. These trends are as follows: increasing phosphate concentrations during the fall and winter months to a high level in January, a sharp decrease over the spring months, and relatively constant concentrations during the summer months. Maximum concentrations of 1.36, 1.31, and 3.23 $\mu\text{g-at/l}$ were obtained for the PIER, INLET, and NAVY sites, respectively, during January 1979. Minimum levels of 0.25, 0.14, and 0.56 $\mu\text{g-at/l}$ were obtained for the PIER, INLET, and NAVY sites during the summer months. The levels obtained during the year for the three sites are also given in appendix table 9.

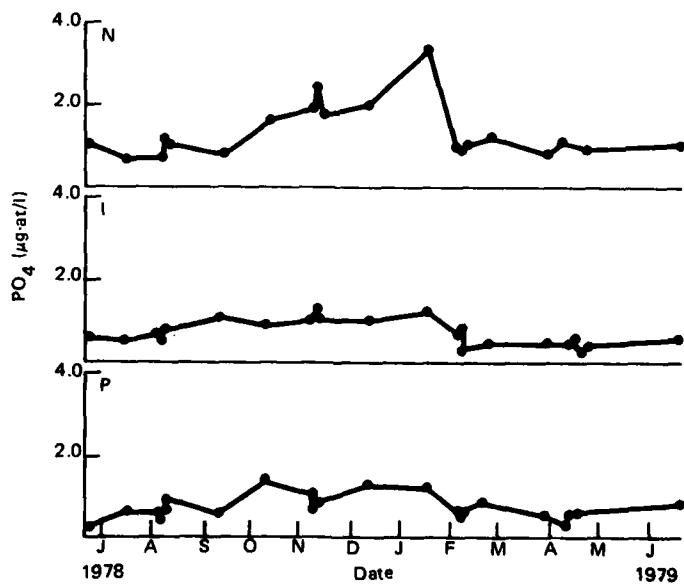


Figure 24. Trends in phosphate concentrations ($\mu\text{g-at PO}_4/\text{l}$) at the PIER (P), INLET (I), and NAVY (N) sites from July 1978 through June 1979.

All phosphate measurements obtained in this study are above the limiting level of 0.25 $\mu\text{g-at/l}$ reported by Goldberg *et al* (1951). These results suggest that phosphate also remained at nonlimiting concentrations during the year.

Silicate

The levels of silicate measured at the three sites over the year are presented in figure 25. The curves in figure 25 indicate that overall levels of silicate at the PIER site were markedly lower than levels characteristic to the INLET and NAVY sites. At the PIER site, levels of silicate varied slightly around a concentration of 7.0 $\mu\text{g-at/l}$. High concentrations of 14.0 and 10.1 $\mu\text{g-at/l}$ were obtained during August and June, respectively. Extreme low concentrations were encountered during February 1979. At this time, silicate concentration was approximately 2.1 $\mu\text{g-at/l}$.

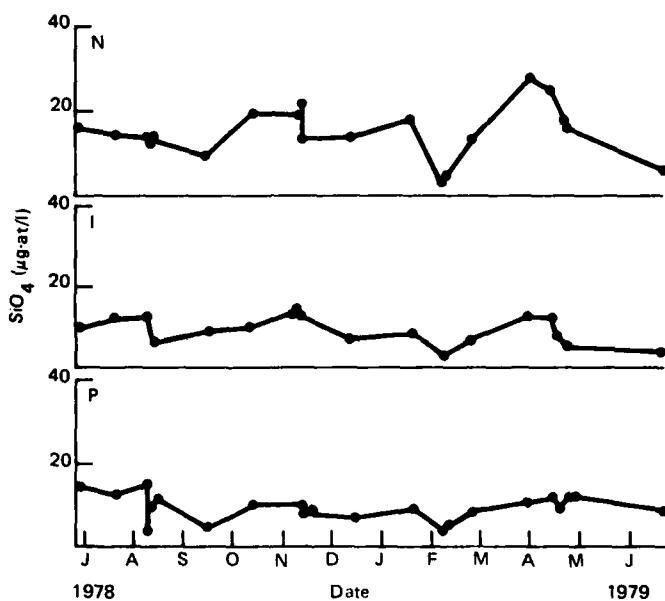


Figure 25. Trends in silicate concentrations ($\mu\text{g-at SiO}_4/\ell$) at the PIER (P), INLET (I), and NAVY (N) sites from July 1978 through June 1979.

At the INLET site, levels of silicate were quite irregular. Peak concentrations were encountered during August 1978 (10.9 $\mu\text{g-at/l}$), late December 1978 (11.4 $\mu\text{g-at/l}$), and April 1979 (11.9 $\mu\text{g-at/l}$). Extreme low concentrations were encountered during late February 1979 (2.7 $\mu\text{g-at/l}$).

The silicate concentrations characteristic of the NAVY site follow a trend similar to that encountered at the INLET site. High concentrations in silicate were obtained for the fall samples (21.8 $\mu\text{g-at/l}$ during November 1978) and for the April 1979 samples (27.0 $\mu\text{g-at/l}$). Extreme low concentrations were encountered during February 1979 (2.1 $\mu\text{g-at/l}$).

In all cases, the levels of silicate measured in San Diego Bay were well above the 0.73 $\mu\text{g-at/l}$ limiting level given by Jorgensen (1953). The results suggest that, as for other

nutrients, silicate remained at nonlimiting levels throughout the year. These conditions of high nutrient concentrations indicate that San Diego Bay is capable of supporting dense populations of phytoplankton.

DISCUSSION

PHYTOPLANKTON-COPPER INTERACTIONS

The results of this research indicate that the ambient levels of copper in seawater were significantly higher at the INLET and NAVY sites than at the PIER site for the soluble fraction of copper in seawater and for the fraction of copper associated with the particulate material. The colloidal fraction and the total copper levels were significantly different at each of the three sites.

Which of these fractions is capable of significant interactions with phytoplankton metabolism is a current subject of controversy among workers in the field. It has been determined that growth inhibition and copper content of plankton cells are not related to total copper concentration (Erickson *et al.* 1970; Sunda and Guillard, 1976). Of the remaining fractions, it is not clear whether it is the cupric ion activity or the copper in inorganic or organic complexes that are more toxic to phytoplankton. Gachter *et al.* (1973) concluded that limiting copper toxicity to only the ionic species is too exclusive. They also indicated that it is reasonable to assume that the free copper ion or its inorganic complexes are more toxic than the organic ones. Sunda and Guillard (1976) strongly suggested that it is only the cupric ion activity that is toxic to phytoplankton. However, they based their conclusions on several assumptions regarding complexed copper and on a calculated ratio for activity of cupric ion to the total copper concentration.

Many other investigators have suggested that it is the copper ion which reacts with the phytoplankton. Mandelli (1969) reported that copper ions bind to the surface of the cells and may interfere with metabolic function. Overnell (1975) suggested that copper ions increase the permeability of the cell. Button and Hosteller (1977) indicated that some phytoplankton have the ability to bind ionic copper to cell walls in such a fashion that it does not readily enter into the protoplasm.

Using the methods employed for copper measurements in this study, it is not possible to separate the effects of the cupric ion from other "soluble" forms of copper on phytoplankton. Measuring seawater under pH 8, unfiltered conditions are believed to yield the ionic fraction of copper plus all copper not complexed or trapped within an "electrical insulator." An "electrical insulator" is defined to be another metal hydroxide, a carbonate or a silicate complex which does not allow reduction of copper (Zirino, personal communication).

The results of this study suggest that it is indeed the soluble fraction that is capable of altering phytoplankton growth. This is indicated in the inverse relationship between soluble copper and productivity and chlorophyll A evident from comparing figures 2, 6, and 7. At all three sites, both productivity and levels of chlorophyll A appear to vary inversely with soluble copper concentration. These relationships are suggested by the correlation coefficients obtained for the PIER data. However, the coefficients obtained for the INLET and NAVY data do not reflect these trends. These results reinforce the hypothesis that the INLET and NAVY assemblages possessed a higher tolerance to copper than did the PIER assemblage.

The phytoplankton characteristics assessed during the year demonstrate several trends. The first is that chlorophyll A levels were similar at the PIER and NAVY sites during the

entire year and slightly elevated at the INLET site only during the spring months. The chlorophyll A levels reported in this study are very similar to levels reported by Lapota and Mannix (1978) for phytoplankton collected from the northern end of San Diego Bay.

Productivity levels also were similar for the phytoplankton assemblages at the PIER and NAVY sites over the entire year, while those at the INLET site were slightly elevated during the spring. This elevation in productivity at the INLET site probably resulted from an increase in biomass, as reflected by elevated chlorophyll A levels during this period. The productivity rates reported in this study are up to three times greater than those reported by Thomas *et al* (1978) for natural phytoplankton assemblages collected off the Scripps Institution of Oceanography pier. An exception to this occurred in January and February 1979. During this time, productivity rates in San Diego Bay were equal to or less than the values given by Thomas *et al*. The elevated productivity rates encountered in San Diego Bay are the result of sheltered conditions and unlimited nutrient levels common to bay and estuarine environments. The low productivity rates encountered during late winter and early spring are probably the result of limited light and adverse weather conditions frequently encountered during this time.

The productivity indices determined for the three sites over the year were essentially the same, although some variability is apparent. Large levels of variability were encountered in the phytoplankton parameters assessed during the intensive sampling sessions. In many cases, the degree of variability encountered among sites is less than that encountered within a site. The similar indices indicate that the assemblages assessed at the three field sites are of equal "fertility," all producing at or near optimum rates of productivity.

The cell counts and genera encountered during the study indicate some differences may exist in community composition among the three sites. Cell counts were highest for the INLET, and decreased at the PIER and NAVY sites (figure 26). On a sample-to-sample,

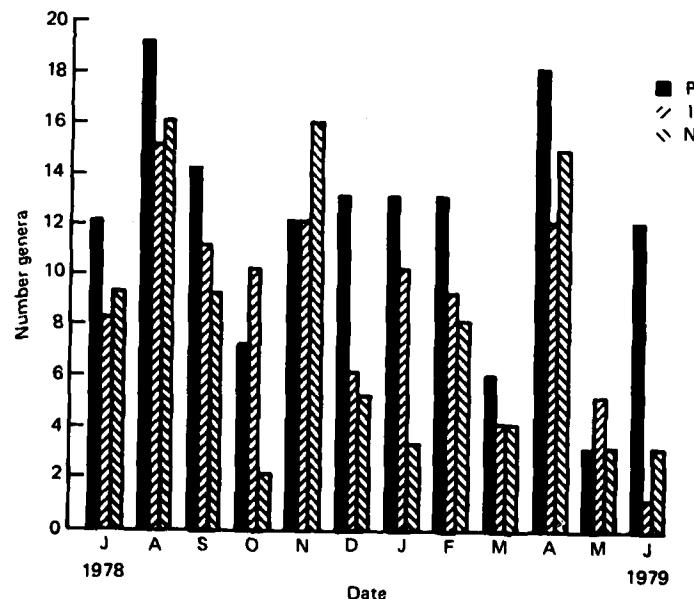


Figure 26. The number of genera encountered per month in phytoplankton samples collected from the PIER(P), INLET(I), and NAVY (N) sites from July 1978 through June 1979.

as well as an overall basis, the PIER site supported the largest number of genera. Fewer genera were encountered at the NAVY site and still fewer at the INLET. These trends are not fully reflected in the diversity indices, however. Indices determined for the PIER assemblage were slightly greater than those determined for either the INLET or NAVY assemblages; however, there is not a significant difference among the three sites.

The percent composition curves of the six most frequently encountered genera indicate a slight difference in dominant phytoplankton among the three sites. Of the six most encountered, *Nitzschia* and *Leptocylindrus* were rarely encountered at the INLET site. *Leptocylindrus* occurred in highest densities during the summer at the PIER and NAVY sites. During the summer, soluble copper levels of 7.0 ppb were present at the INLET and NAVY sites. As *Leptocylindrus* was observed to exist in the presence of elevated copper levels at the NAVY site, it is felt that the absence of this genus from the INLET probably is the result of two possible factors: 1) the tidal activity during the summer may have restricted *Leptocylindrus* from the INLET area, or 2) the toxic fraction of copper may have exceeded its tolerance levels at the INLET site.

Nitzschia occurred primarily at the NAVY and PIER sites during the spring. At this time, soluble copper levels appeared to reach minimum concentrations at all three sites. Once again, the absence of *Nitzschia* from the INLET may have been the result of several variables. Steeman Nielsen and Wium-Andersen (1971) indicated extreme sensitivity of *Nitzschia palea* to copper levels greater than 1.2 $\mu\text{g Cu/l}$. This may be extrapolated to the San Diego Bay INLET area. As *Nitzschia* moved into the bay toward the INLET area from uncontaminated coastal areas, it would pass through an increasing gradient of copper concentrations. Because of this, *Nitzschia* may be excluded before it is carried as far into San Diego Bay as the INLET site. This increasing gradient of copper also may restrict other sensitive phytoplankton from entering the area. Many of the genera encountered less frequently in this study are known to be highly sensitive to low concentrations of copper. The marine dinoflagellates *Prorocentrum micans* and *Gymnodinium splendens* exhibited decreased cell division, chlorophyll A levels, and uptake of carbon when exposed to copper levels that exceeded 5.0 ppb (Saifullah, 1978). Anderson and Morel (1978) reported that photosynthetic carbon fixation by *Gonyaulax tamarensis*, as well as loss of motility, resulted when copper levels in natural waters exceeded levels which left other algae relatively unaffected.

Copper levels as low as 1.0 ppb are reported to inhibit photosynthetic activity in the diatom *Thalassiosira pseudonana* (Erickson, 1972; Davey *et al.* 1973). Berland *et al.* (1977) and Morel *et al.* (1978) indicated that *Skeletonema costatum* is relatively insensitive in terms of division rate, maximum yield growth, and ^{14}C -uptake to cupric ion activity equal to 1.0 ppb.

Several investigators have reported that the diversity of phytoplankton communities declines with increasing levels of copper. Steeman Nielsen and Laursen (1976), Harrison *et al.* (1977), Thomas *et al.* (1977), and Thomas and Seibert (1977) suggested that one effect of introducing this pollutant into the marine environment will be a decrease in the taxonomic diversity of phytoplankton, with a resulting dominance of more resistant species.

This trend was observed in the laboratory tolerance test conducted for this study. The INLET assemblage initially consisted of six genera, of which the dominant form was an unidentified flagellate, genus #5. The results suggest that this flagellate has a relatively high tolerance to copper and thus is able to withstand elevated copper levels. On the other hand, the PIER assemblage initially consisted of 12 - 15 genera, with *Nitzschia* as the dominant form. As copper concentrations increased, the number of genera decreased to four. While *Nitzschia* was still the dominant form, its densities were extremely low. This suggests that the members of the PIER assemblage were less tolerant to elevated copper than those of the INLET assemblage.

In order to demonstrate clearly the development of a dominant, resistant phytoplankton species in copper-contaminated water, it would be necessary to conduct a longer bioassay experiment than used in this study. A minimum of 14 days probably would be required. After this period, it would be possible to observe shifts in the dominant species under contaminated conditions.

The addition of copper to a bay above normal concentrations may have various effects on its biological conditions. High levels of copper may severely alter lower trophic levels so that only a few tolerant species remain. This could have serious adverse affects on higher trophic levels if species required by grazers were eliminated. However, extreme effects such as these are not probable. Rather, alterations in community composition resulting in a smaller number of species is most likely to result. Such changes in the lower trophic levels may or may not affect higher trophic levels. This depends on the nature and degree of change among the phytoplankton.

EFFECTS OF TEMPERATURE AND LIGHT

Temperature is an important factor regulating photosynthesis. Strickland (1965) indicated that the effect of temperature on photosynthesis is generally small over a range of 3°C or more on each side of the "optimum" temperature for a given species. Since there is a fairly narrow temperature range in San Diego Bay, temperature probably is not a controlling factor in the phytoplankton-copper relationships investigated.

However, light appears to be one of the primary factors responsible for the trends in phytoplankton growth observed during this study. This is evident from the trends in chlorophyll A and productivity observed during the year. Levels of chlorophyll A and productivity rates were highest during the spring and summer months. These are the months during which San Diego receives maximum light levels and greatest day length. Chlorophyll A levels and productivity rates were lowest during the winter months when light availability was at its minimum.

These results indicate that the phytoplankton assemblages in San Diego Bay are highly correlated with light levels. The fact that productivity indices were similar for the three sites indicates light conditions probably were essentially the same at the three sites within San Diego Bay.

EFFECTS OF SALINITY

Within a range of 25-35 ppt, the effects of varying salinity on photosynthesis of marine phytoplankton are likely to be slight (Strickland, 1965). Salinity levels at the three sites monitored in San Diego Bay varied only 3-8 ppt around a mean concentration of 32.6 ppt during the year. The results of multiple partial correlation analysis do not indicate any significant correlations between salinity and phytoplankton growth or diversity. This lack of significant correlations, combined with the narrow range of salinities encountered, suggests that variations in salinity do not affect phytoplankton growth or copper concentrations significantly.

EFFECTS OF pH

Riley and Skirrow (1965) suggested that there are very few fluctuations in the pH of seawater, with values falling outside of the range 7.8-8.3 only under exceptional circumstances. The increases in pH were a result of photosynthetic activity and utilization of CO₂. These generally occurred during the hours of daylight. Marked decreases in pH have been observed

by Ibert and Hood (1963) during periods of heavy rainfall. Decreases of as much as 1.5 pH units have been recorded in shallow water masses during such periods.

The pH of seawater measured at the three test sites fluctuated irregularly over the year. The marked decreases encountered may have been associated with periods of heavy rainfall, as suggested by Ibert and Hood (1963). However, they probably reflect patchiness in phytoplankton distribution and photosynthetic activity (Zirino, personal communication). The pH measurements reported by Lenz (1976) for San Diego Bay range between 7.9 and 8.02, while Zirino reported values as high as 8.3 (personal communication). The pH in bay environments is highly dependent on photosynthetic activity and fresh water added to the system. It is felt that the variation in pH measurements obtained during the year primarily reflect photosynthetic activity. Variations throughout the year probably were the result of changes in phytoplankton assemblages.

TIDAL INFLUENCE

The degree of circulation attributable to tidal activity is an important environmental factor in bay and estuarine environments. Minimal water exchange because of restricted flow may result in isolated phytoplankton communities. The PIER site lies directly in the main channel of San Diego Bay and therefore is well flushed. In contrast, the INLET site is in a well protected cove that, according to the model prepared by Lenz (1976), has severely restricted tidal flushing. The model indicates that the NAVY site is flushed to a lesser degree than the PIER, but more so than the INLET site.

Such restricted tidal activity may be an important factor in terms of its effects on phytoplankton diversity and the concentrations of trace metals. However, circulation studies were not performed as part of this investigation and thus the effects of circulation on phytoplankton dynamics may only be implied.

Zirino *et al* (1978) found that copper levels varied from 3.6 to 0.5 ppb at a given site in San Diego Bay over a two-day period. They attributed these fluctuations to tidal activity and suggested that during low tides, copper-contaminated bay water is brought past the sample site, thus resulting in elevated copper levels during that part of the tidal cycle. It follows that the "clean" ocean water carried by incoming tides would replace this contaminated water.

Tidal activity may also deliver coastal phytoplankton into San Diego Bay as far as the NAVY site and carry the bay assemblages past the PIER site. If tidal exchange is very slight in the INLET area, one might expect that the INLET site would support fewer genera of coastal phytoplankton than are encountered at the PIER and NAVY sites.

NUTRIENTS

The rate of photosynthesis by phytoplankton is governed primarily by light and nutrients. R. W. Eppley of the Scripps Institution of Oceanography suggested that nutrients in San Diego Bay are replenished faster than they are utilized (personal communication), which would indicate a nutrient-unlimited environment. The bay derives nutrients from the decomposition of sea life and from nutrient-rich waste products washed into the bay from industries and other sources.

The results obtained in this investigation indicate that each site had the potential to support active phytoplankton communities. Results described in the sections on phytoplankton characteristics indicate that the PIER, INLET, and NAVY sites did support phytoplankton communities of equal fertility or photosynthetic activity per unit biomass. These results also suggest that the INLET and NAVY assemblages were composed of fewer genera than the

PIER assemblage. This difference in community composition probably was not the result of nutrient supply but rather the result of a limiting external factor, such as copper.

CONCLUSIONS

The factors regulating phytoplankton growth, productivity and diversity are numerous and interrelated. Light and nutrient availability are of great importance. Phytoplankton require certain elements in minute quantities. Included among these are trace amounts of copper. However, when present in excess, copper can be toxic to phytoplankton. The results of this study suggest that it is the soluble fraction of copper that has the capability to affect phytoplankton metabolism. However, more detailed studies are required to demonstrate this fully.

In the INLET and NAVY regions of San Diego Bay, where ship maintenance occurred regularly, levels of soluble copper were significantly higher than at the PIER site, which was free of heavy boat traffic and maintenance activities. The average concentration of copper at the PIER site was less than 1.0 ppb while copper levels at the INLET and NAVY sites averaged 4.0 ppb.

Although the INLET and NAVY sites were characterized by significantly higher copper levels than the PIER site, phytoplankton productivity and biomass were not reduced. In contrast, the INLET site supported a significantly higher biomass of phytoplankton than the PIER or NAVY sites. This also was accompanied by significantly higher levels of productivity. However, the productivity indices, which provide a measure of the fertility of the assemblage, were similar at the three sites. This indicates that the three phytoplankton assemblages were of equal fertility or vitality per unit biomass. It further suggests that the phytoplankton from the INLET and NAVY sites had a relatively high tolerance to high copper levels.

Diversity indices determined for the three communities showed no significant differences. However, by examining the number of genera present per month at each site as well as the composition of those phytoplankton communities, it was evident that the INLET and NAVY sites consistently supported fewer genera than the PIER site. Phytoplankton genera absent from these sites are among those reported to be sensitive to copper toxicity. This suggests that tidal activity may not be restricting numerous phytoplankton genera from entering the INLET and NAVY sites but that, instead, elevated copper levels present there are selecting against the most sensitive genera. As a result, only the more tolerant forms of phytoplankton are present.

These trends are supported by the results of the laboratory toxicity experiment. The phytoplankton taken from the INLET site exhibited slight decreases in productivity and biomass under conditions of elevated copper. The phytoplankton taken from the PIER site, however, exhibited a drastic decrease in productivity and biomass at copper levels above 5 ppb. Under conditions of ambient copper levels, the INLET assemblage was composed of six genera. The number of genera decreased to four as copper levels reached 40 ppb in the experiment. The PIER assemblage, under similar conditions, was composed of 12 genera. This assemblage decreased to four genera as the copper level in the experiment increased to 40 ppb. These results suggest two trends: 1) the phytoplankton taken from the INLET site have a tolerance to elevated copper levels that permits active productivity and high biomass; and 2) the phytoplankton taken from the PIER site are not able to withstand higher concentrations of copper, and exhibit decreased productivity, biomass, and diversity as copper concentrations increase.

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APPENDIX

<u>Date</u>	<u>Site</u>	<u>Time</u>	<u>Site</u>	<u>Time</u>	<u>Site</u>	<u>Time</u>
7/17/78	1P	1015	1I	1015	1N	1100
8/08/78	2P	0940	2I	0910	2N	0945
8/28/78	3P	0925	3I	0900	3N	0945
8/29/78	4P	0905	4I	0840	4N	0808
8/30/78	5P	0705	5I	0640	5N	0806
8/30/78	6P	1100	6I	1050	6N	--
8/30/78	7P	1510	7I	1450	7N	1610
8/31/78	8P	0920	8I	0905	8N	0900
10/02/78	9P	1010	9I	0950	9N	1005
10/30/78	10P	0805	10I	0745	10N	0810
11/26/78	11P	0950	11I	1011	11N	1015
11/27/78	12P	0730	12I	0750	12N	0830
11/27/78	13P	1218	13I	1242	13N	1215
11/27/78	14P	1533	14I	1552	14N	1616
11/28/78	15P	0735	15I	0725	15N	--
11/29/78	16P	1150	16I	1205	16N	1148
12/20/78	17P	0835	17I	0820	17N	0830
2/01/79	18P	0820	18I	0825	18N	0830
2/19/79	19P	0835	19I	0820	19N	0830
2/20/79	20P	0820	20I	0805	20N	0800
2/21/79	21P	0745	21I	0730	21N	--
2/21/79	22P	1145	22I	1133	22N	1110
2/21/79	23P	1445	23I	1430	23N	--
2/22/79	24P	0830	24I	0815	24N	0803
3/07/79	25P	0815	25I	0800	25N	0900
4/11/79	26P	0805	26I	0740	26N	0815
4/24/79	27P	0820	27I	0805	27N	0800
4/26/79	28P	0815	28I	0800	28N	0825
5/02/79	29P	0915	29I	0900	29N	0800
5/04/79	30P	0840	30I	0825	30N	0815
6/26/79	31P	0820	31I	0805	31N	0900

Appendix Table 1. Date and time of sample collection at the PIER, INLET, and NAVY sites.

<u>Sample No.</u>	<u>Date</u>	<u>Time</u>	<u>Conditions</u>
1	7/17/78	1015	Overcast
2	8/08/78	0940	Cloudy and windy
3	8/28/78	0925	Overcast, very calm
4	8/29/78	0905	Overcast
5	8/30/78	0705	Overcast, clearing
6	8/30/78	1100	Overcast
7	8/30/78	1510	Clear and sunny
8	8/31/78	0920	Clear and sunny
9	10/02/78	1010	Overcast, foggy
10	10/30/78	0805	Overcast, windy
11	11/26/78	0950	Sunny, cool, slight surface chop
12	11/27/78	0730	Sun rising, very flat
13	11/27/78	1218	Calm, sunny
14	11/27/78	1533	Sunny, cool
15	11/28/78	0735	Sunny, flat
16	11/29/78	1150	Sunny, slight chop
17	12/20/78	0835	Sunny, flat, cool
18	2/01/79	0820	Rain prior three days, cool, cloudy
19	2/19/79	0835	Overcast, grey
20	2/20/79	0820	Clearing
21	2/21/79	0745	Raining
22	2/21/79	1145	Clearing, high clouds
23	2/21/79	1445	Sunny
24	2/22/79	0830	Slightly overcast
25	3/07/79	0815	Sunny, warm
26	4/11/79	0805	Overcast, slight chop
27	4/24/79	0820	Sunny, oil on water at INLET
28	4/26/79	0815	Sunny, calm
29	5/02/79	0915	Overcast, choppy
30	5/04/79	0840	Overcast, cool
31	6/26/79	0820	Slightly overcast

Appendix Table 2. General weather conditions at time of sample collection.

Sample	PIER				INLET				NAVY			
	Part	Solb	Total	Coll	Part	Solb	Total	Coll	Part	Solb	Total	Coll
1	2.3	0.4	0.8	1.6	2.5	3.7	7.0	4.1	5.2	1.7	3.2	0.8
2	0.7	1.0	4.0	2.6	1.5	2.0	9.6	9.9	2.4	4.3	21.8	12.6
3	1.5	0.7	1.7	2.5	1.9	4.6	14.1	9.4	2.7	9.5	22.6	23.2
4	1.4	2.2	3.1	1.2	2.0	4.7	8.3	6.3	1.5	6.0	12.4	4.8
5	1.5	0.2	3.1	0.9	2.0	6.5	19.1	9.3	1.8	2.3	7.5	3.5
6	1.4	0.9	3.2	1.2	2.0	6.8	15.8	11.2	--	--	--	--
7	1.5	1.0	1.2	1.0	1.9	7.4	18.4	17.9	1.4	4.8	6.4	5.2
8	1.5	1.0	2.3	1.3	1.9	5.9	14.2	15.3	2.8	2.8	9.8	4.0
9	1.8	2.0	2.1	1.5	2.4	5.7	9.5	4.5	3.5	3.0	9.3	4.5
10	2.1	0.7	0.4	1.3	2.5	2.6	5.1	3.9	1.3	4.7	5.0	2.9
11	1.3	0.9	3.1	1.6	1.6	4.0	9.8	5.9	1.2	2.5	6.0	4.1
12	1.4	0.7	1.1	0.4	1.9	3.1	6.8	5.2	1.8	2.7	4.9	3.0
13	1.6	2.4	7.9	5.1	1.3	0.8	2.8	1.2	1.7	4.4	7.6	7.0
14	1.5	5.8	8.4	8.5	1.3	1.8	1.7	0.9	1.9	4.4	8.4	7.4
15	1.0	0.6	0.8	1.1	5.6	2.5	6.9	3.3	--	--	--	--
16	1.6	0.9	2.7	2.3	1.5	3.6	6.5	1.2	2.3	2.4	3.1	2.2
17	1.2	0.9	1.8	2.4	1.5	5.8	8.6	9.7	1.5	2.7	4.5	5.6
18	2.0	0.8	1.5	0.9	1.6	2.4	6.2	6.2	3.9	1.5	3.7	2.9
19	1.8	0.8	1.6	0.1	2.6	1.8	5.4	3.3	2.0	0.8	2.1	2.1
20	1.9	0.5	1.9	1.3	2.8	3.6	6.2	4.0	1.9	1.4	2.2	2.3
21	2.2	0.5	2.6	1.4	2.9	2.6	8.3	1.8	--	--	--	--
22	1.8	0.5	1.0	1.7	2.4	3.3	4.1	5.6	2.7	1.7	4.6	4.1
23	1.0	0.7	2.1	1.0	2.5	3.2	4.2	4.0	--	--	--	--
24	2.2	0.5	0.8	1.4	2.4	2.7	6.5	6.8	2.3	1.2	2.6	2.9
25	1.8	0.9	1.2	1.8	2.5	1.8	6.8	6.5	2.2	3.1	5.4	3.7
26	1.8	0.5	0.7	0.7	2.4	1.5	8.9	2.9	1.6	1.4	2.4	1.2
27	2.0	0.2	0.3	0.7	2.3	1.5	6.4	3.3	1.8	1.7	2.8	2.3
28	1.8	0.1	0.7	0.7	2.5	2.7	7.8	6.2	2.1	2.8	3.5	2.1
29	1.8	0.1	0.7	0.7	2.3	2.9	5.3	4.1	2.1	3.2	3.6	5.7
30	2.2	1.0	2.2	3.6	2.6	2.4	6.1	6.0	3.3	2.5	5.7	5.8
31	2.3	1.0	2.0	1.3	2.5	2.7	7.6	7.6	2.8	3.7	9.7	6.4

Appendix Table 3. Individual measurements of copper associated with particulate material (PART) in $\mu\text{g/l}$, soluble copper (SOLB) in ppb, colloidal copper (COLL) in ppb, and total copper (TOTAL) in ppb for seawater samples collected from the PIER, INLET, and NAVY sites from July 1978 through June 1979.

Sample	PIER				INLET				NAVY			
	Prod	Chla	PI	Divr	Prod	Chla	PI	Divr	Prod	Chla	PI	Divr
1	22.50	4.46	5.04	0.837	21.04	4.46	4.72	0.795	43.52	1.90	22.85	0.836
2	111.15	2.04	54.37	0.837	74.95	2.93	25.61	0.551	106.1	3.11	34.08	0.496
3	56.68	2.65	21.40	0.747	54.81	2.32	23.50	0.634	36.44	1.90	19.13	0.656
4	38.95	2.79	13.97	0.768	37.56	2.32	16.17	0.273	52.39	2.04	25.63	0.690
5	14.69	1.39	10.54	0.700	30.79	3.25	9.47	0.248	18.35	1.67	10.97	0.559
6	22.89	1.02	22.39	--	38.49	2.09	18.41	--	--	--	--	--
7	28.48	1.95	14.60	--	48.83	1.95	25.03	--	24.13	2.37	10.18	--
8	23.58	1.77	13.36	0.475	34.49	2.93	11.78	0.179	30.31	2.17	13.94	0.629
9	27.24	1.05	25.86	0.558	26.80	1.05	25.52	0.756	26.17	1.44	18.17	0.769
10	12.98	1.10	11.81	0.785	46.85	2.09	22.41	0.563	29.00	1.73	16.78	0.182
11	5.80	0.59	9.86	0.019	14.50	2.94	4.93	0.453	10.95	1.27	8.60	0.225
12	13.32	0.68	19.55	0.609	33.20	1.49	22.33	0.680	7.79	0.98	7.98	0.115
13	25.32	1.41	17.97	--	10.38	0.82	12.64	--	3.95	0.74	5.31	--
14	19.66	2.32	8.46	--	13.51	1.19	11.34	--	-1.62	1.03	-1.57	--
15	8.18	1.12	7.34	0.685	20.22	2.32	8.71	0.593	--	--	--	--
16	26.08	1.21	21.69	0.429	13.26	1.81	7.32	0.371	38.61	1.25	30.78	0.325
17	6.67	0.77	8.61	0.499	16.12	1.77	9.13	0.625	24.26	0.70	34.82	0.094
18	10.66	1.02	10.43	0.634	17.80	1.59	11.17	0.675	3.40	0.67	5.07	0.453
19	5.17	0.56	9.28	0.128	72.32	2.97	24.32	0.391	10.91	0.63	17.26	0.091
20	7.48	3.26	2.29	0.552	60.01	3.20	18.77	0.249	7.79	0.75	10.34	0.341
21	12.89	1.16	11.10	0.601	75.81	3.26	23.24	0.007	--	--	--	--
22	12.11	1.04	11.64	--	29.08	3.07	9.48	--	6.32	0.81	7.81	--
23	10.10	1.72	5.87	--	26.14	5.11	5.11	--	--	--	--	--
24	8.59	0.98	8.81	0.757	43.34	4.23	10.25	0.051	22.18	1.41	15.71	0.131
25	24.16	1.39	17.34	0.487	68.12	6.75	10.10	0.405	10.50	0.88	11.89	0.487
26	13.62	1.55	8.78	0.865	24.97	6.75	3.70	0.110	16.45	2.17	7.60	0.900
27	44.12	2.42	18.26	0.653	72.62	4.34	16.74	0.626	19.58	2.01	9.73	0.184
28	32.73	2.67	12.24	0.641	54.97	3.53	15.57	0.618	45.31	3.78	11.99	0.106
29	36.65	2.76	13.30	0.342	41.27	2.55	16.21	0.714	52.56	2.67	19.71	0.545
30	40.39	2.76	14.65	0.285	44.96	3.08	14.62	0.487	23.17	2.51	9.13	0.666
31	60.86	2.89	21.03	0.268	38.23	1.77	21.66	0.000	16.22	0.93	17.45	0.364

Appendix Table 4. Individual measurements of primary productivity (PROD) in $\mu\text{g C/l/h}$, chlorophyll A (CHLA) in mg/m^3 , productivity index (PI), and diversity index (DIVER) for phytoplankton assemblages taken from the PIER, INLET, and NAVY sites from July 1978 through June 1979.

DINOFLAGELLATES

SAMPLE NUMBER

PIER

<u>Genus</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>	<u>11</u>	<u>12</u>	<u>13</u>	<u>14</u>
<i>Gymnodinium</i>	0	0	5	27	18	0	0	1	0	0	0	0	0	0
<i>Ceratium</i>	15	8	4	0	4	0	3	0	2	0	0	0	0	1
<i>Dinophysis</i>	1	0	3	0	4	0	1	0	0	0	0	0	0	0
<i>Gonyaulax</i>	11	30	15	0	14	3	12	5	3	3	6	0	2	0
<i>Noctulica</i>	0	2	0	0	12	1	0	2	0	0	0	0	0	0
<i>Peridinium</i>	9	12	12	1	18	10	2	0	3	0	0	0	0	7
<i>Prorocentrum</i>	57	16	25	23	268	83	83	55	0	0	0	0	0	0

INLET

<i>Gymnodinium</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Ceratium</i>	4	0	6	0	2	2	8	0	24	0	0	0	0	1
<i>Dinophysis</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Gonyaulax</i>	15	6	0	2	0	5	6	2	380	13	18	23	0	0
<i>Noctulica</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Peridinium</i>	6	3	2	0	0	0	10	1	12	10	15	34	0	2
<i>Prorocentrum</i>	30	44	3	8	4	0	20	9	0	0	6	9	0	1

NAVY

<u>Genus</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>	<u>11</u>	<u>12</u>	<u>13</u>	<u>14</u>
<i>Gymnodinium</i>	0	3	15	0	0	0	0	0	0	0	0	0	0	1
<i>Ceratium</i>	1	0	0	1	0	0	0	0	0	0	0	0	0	0
<i>Dinophysis</i>	0	0	0	0	0	0	0	1	0	0	0	0	1	0
<i>Gonyaulax</i>	48	286	0	8	7	4	19	9	9	0	2	1	0	0
<i>Noctulica</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Peridinium</i>	21	38	0	20	4	2	6	0	0	0	2	2	0	1
<i>Prorocentrum</i>	0	21	3	101	1	6	15	6	2	0	1	0	1	2

PIER

	<u>15</u>	<u>16</u>	<u>17</u>	<u>18</u>	<u>19</u>	<u>20</u>	<u>21</u>	<u>22</u>	<u>23</u>	<u>24</u>	<u>25</u>	<u>26</u>	<u>27</u>	<u>28</u>
<i>Gymnodinium</i>	0	0	0	0	0	0	0	2	0	1	0	0	0	1
<i>Ceratium</i>	0	0	0	0	0	0	1	0	0	0	0	4	1	2
<i>Dinophysis</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Gonyaulax</i>	4	2	1	1	1	0	0	0	1	1	0	2	1	2
<i>Noctulica</i>	0	0	0	0	0	0	2	1	1	0	0	0	0	0
<i>Peridinium</i>	0	0	0	0	1	0	0	0	1	1	0	4	3	4
<i>Prorocentrum</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Appendix Table 5. Estimated density (number of cells $\times 10^2/\text{liter}$) of phytoplankton taken at the PIER, INLET, and NAVY sites from July 1978 through June 1979.

Genus	INLET													
	15	16	17	18	19	20	21	22	23	24	25	26	27	28
<i>Gymnodinium</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Ceratium</i>	0	0	0	0	0	0	0	0	0	1	0	1	0	0
<i>Dinophysis</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Gonyaulax</i>	32	0	3	1	0	0	0	0	0	1	0	1	2	0
<i>Noctulica</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Peridinium</i>	133	0	0	0	1	0	0	0	0	0	0	3	0	0
<i>Prorocentrum</i>	1	0	0	55	0	0	0	0	0	0	0	0	0	0
NAVY														
<i>Gymnodinium</i>	0	0	1	0	0	0	0	0	0	0	0	0	0	0
<i>Ceratium</i>	0	0	0	0	1	0	0	0	0	0	0	1	0	0
<i>Dinophysis</i>	0	0	0	0	0	0	0	0	0	0	0	0	6	0
<i>Gonyaulax</i>	0	3	1	0	0	0	0	0	0	0	0	0	1	0
<i>Noctulica</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Peridinium</i>	0	0	0	0	1	1	0	0	0	1	0	0	1	0
<i>Prorocentrum</i>	0	2	0	0	0	0	0	0	0	0	0	1	0	0
PIER					INLET			NAVY						
Genus	29	30	31	29	30	31	29	30	31	29	30	31	29	30
<i>Gymnodinium</i>	0	0	1	0	0	0	0	0	0	0	0	0	0	0
<i>Ceratium</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Dinophysis</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Gonyaulax</i>	0	0	0	0	7	0	0	0	0	0	0	0	0	0
<i>Noctulica</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Peridinium</i>	0	0	1	0	0	0	0	0	0	0	0	0	0	0
<i>Prorocentrum</i>	0	0	1	0	0	0	0	0	0	0	0	0	0	0

Appendix Table 5. (Continued).

Genus	DIATOMS PIER													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
<i>Asterionella</i>	0	1	0	0	0	0	0	0	0	0	0	0	0	0
<i>Biddulphia</i>	0	0	1	0	0	0	0	0	0	0	0	0	0	0
<i>Ceratulina</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Chaetoceros</i>	12	0	14	10	40	0	0	85	13	20	3760	179	258	325
<i>Coscinodiscus</i>	3	10	4	1	0	1	4	0	2	0	0	0	0	1
<i>Ditylum</i>	0	0	0	0	0	0	0	0	8	0	4	1	1	0
<i>Eucampia</i>	0	0	3	0	0	0	0	0	2	0	0	0	0	0
<i>Leptocylindrus</i>	9	0	320	43	328	32	8	44	527	0	0	0	0	0
<i>Licomorpha</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Navicula</i>	2	0	0	0	0	0	0	0	4	9	2	0	0	0
<i>Nitzschia</i>	36	18	170	46	270	86	30	1100	19	35	13	78	0	1
<i>Rhizosolenia</i>	0	0	8	39	2	0	0	0	349	15	4	68	12	12
<i>Skeletonema</i>	8	3	10	160	76	30	13	0	0	0	0	0	60	30
<i>Thalassiosira</i>	0	0	0	1	0	0	0	0	0	0	0	0	8	0
<i>Thalassiothrix</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Achnanthes</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Streptotheca</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Thalassionema</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Pleurosigma</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Diatom #12</i>	0	0	75	189	1016	456	363	746	7	12	6	4	92	153
<i>Stephanophysix</i>	0	3	0	0	0	0	0	0	0	0	0	0	0	0
<i>Diatom #19</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Suriella</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Genus #5</i>	25	0	0	1	6	2	0	4	10	3	3	0	1	0

Appendix Table 5. (Continued).

	INLET													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
<i>Asterionella</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Biddulphia</i>	0	0	0	0	0	0	0	0	0	0	0	0	4	0
<i>Ceratulina</i>	0	0	3	0	0	0	0	0	0	0	0	0	0	8
<i>Chaetoceros</i>	1	0	417	64	0	49	9	0	38	346	259	355	24	360
<i>Coscinodiscus</i>	0	0	1	0	2	0	0	0	30	21	0	1	0	1
<i>Ditylum</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	1
<i>Eucampia</i>	0	0	0	0	0	0	0	4	0	0	0	0	0	0
<i>Leptocylindrus</i>	2	0	105	154	28	54	270	22	30	0	0	0	0	0
<i>Licomorpha</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Navicula</i>	0	0	0	0	2	0	0	0	0	0	0	0	3	3
<i>Nitzschia</i>	29	6	118	124	0	125	250	103	54	262	0	0	9	10
<i>Rhizosolenia</i>	0	0	5	6	50	0	10	10	68	4	0	14	10	13
<i>Skeletonema</i>	0	4	92	60	64	12	0	0	0	1367	9	51	10	0
<i>Thalassiosira</i>	20	4	0	0	0	0	0	0	10	0	0	19	4	0
<i>Thalassiothrix</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Achnanthes</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Streptothecea</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Thalassionema</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Pleurosigma</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Diatom #12</i>	0	0	868	2402	1004	40	2150	1650	144	139	33	194	1	5
<i>Stephanophysix</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Diatom #19</i>	0	0	0	0	0	0	6	0	0	17	13	10	0	0
<i>Suriella</i>	0	0	0	0	0	0	0	0	0	0	0	0	1	0
<i>Genus #5</i>	0	0	1	10	6	15	0	24	74	3	2	16	0	0

Appendix Table 5. (Continued).

	NAVY													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
<i>Asterionella</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Biddulphia</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	8
<i>Ceratulina</i>	0	0	0	0	0	0	0	0	0	0	12	0	15	16
<i>Chaetoceros</i>	28	0	4	137	0	36	20	0	108	53	397	660	254	193
<i>Coscinodiscus</i>	6	1	0	5	8	0	1	4	0	0	3	0	0	2
<i>Ditylum</i>	0	0	0	0	0	0	0	0	0	0	0	2	0	0
<i>Eucampia</i>	0	0	0	7	0	0	0	0	9	0	0	0	0	0
<i>Leptocylindrus</i>	22	0	73	199	75	135	0	4	53	6	19	0	0	0
<i>Licromorpha</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Navicula</i>	0	0	0	0	0	1	0	0	0	0	0	1	1	0
<i>Nitzschia</i>	21	5	25	56	44	0	58	66	33	0	0	1	0	0
<i>Rhizosolenia</i>	0	0	0	52	23	3	100	131	7	0	0	9	0	6
<i>Skeletonema</i>	70	6	3	1086	292	0	30	96	106	0	0	0	0	0
<i>Thalassiosira</i>	46	678	0	0	2	0	2	0	0	0	0	8	0	0
<i>Thalassiothrix</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Achnanthes</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Streptothecea</i>	0	0	0	0	1	0	0	0	0	0	0	0	0	0
<i>Thalassionema</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Pleurosigma</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Diatom #12</i>	0	0	12	705	718	501	236	400	181	0	14	0	0	0
<i>Stephanophysix</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Diatom #19</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Suriella</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Genus #5</i>	0	0	0	0	0	4	0	0	0	0	0	0	0	0

Appendix Table 5. (Continued).

PIER

	<u>15</u>	<u>16</u>	<u>17</u>	<u>18</u>	<u>19</u>	<u>20</u>	<u>21</u>	<u>22</u>	<u>23</u>	<u>24</u>	<u>25</u>	<u>26</u>	<u>27</u>	<u>28</u>
<i>Asterionella</i>	13	0	0	8	70	4	6	82	169	0	63	0	0	0
<i>Biddulphia</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Ceratulina</i>	43	0	23	0	0	0	0	0	0	0	0	0	0	0
<i>Chaetoceros</i>	151	49	0	99	0	0	16	0	0	0	475	0	577	546
<i>Coscinodiscus</i>	6	0	0	3	0	0	0	0	0	1	2	0	2	1
<i>Ditylum</i>	1	1	1	0	0	0	0	0	0	0	3	0	0	0
<i>Eucampia</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	61
<i>Leptocylindrus</i>	0	0	0	9	0	0	3	0	0	0	0	0	42	48
<i>Licomorpha</i>	0	1	0	0	0	0	0	0	0	0	0	0	0	0
<i>Navicula</i>	0	2	1	1	0	0	0	0	1	0	0	5	3	0
<i>Nitzschia</i>	35	0	0	2	0	1	0	0	2	2	3	5	1120	1227
<i>Rhizosolenia</i>	16	10	0	0	3	0	5	0	0	0	0	0	43	174
<i>Skeletonema</i>	0	0	0	126	0	0	0	0	0	0	0	0	398	142
<i>Thalassiosira</i>	0	0	0	14	0	0	0	0	0	0	0	0	8	20
<i>Thalassiothrix</i>	0	0	0	0	0	0	0	0	0	0	0	0	18	0
<i>Achnanthes</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Streptotheca</i>	0	0	0	0	0	0	0	0	0	0	0	0	10	10
<i>Thalassionema</i>	0	0	0	0	0	0	0	0	0	0	0	0	20	36
<i>Pleurosigma</i>	0	0	0	0	0	0	0	0	0	0	0	1	0	2
<i>Diatom # 12</i>	21	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Stephanophysix</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Diatom # 19</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Suriella</i>	0	0	0	2	0	2	0	1	6	0	0	0	0	0
<i>Genus # 5</i>	0	1	1	8	1	0	13	49	13	4	159	2	1	1

Appendix Table 5. (Continued).

	INLET													
	<u>15</u>	<u>16</u>	<u>17</u>	<u>18</u>	<u>19</u>	<u>20</u>	<u>21</u>	<u>22</u>	<u>23</u>	<u>24</u>	<u>25</u>	<u>26</u>	<u>27</u>	<u>28</u>
<i>Asterionella</i>	0	0	0	2	526	704	772	942	779	371	56	0	0	0
<i>Biddulphia</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Ceratulina</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Chaetoceros</i>	477	200	0	121	150	102	0	0	40	0	59	0	12	6
<i>Coscinodiscus</i>	0	0	1	2	0	0	0	0	0	0	0	0	1	0
<i>Ditylum</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Eucampia</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Leptocylindrus</i>	0	0	0	3	0	0	0	0	0	0	0	4	0	0
<i>Licromorpha</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Navicula</i>	0	0	2	3	0	0	0	0	1	0	0	0	1	0
<i>Nitzschia</i>	4	0	2	2	0	15	0	0	0	1	1	0	2	4
<i>Rhizosolenia</i>	13	14	6	0	16	0	0	0	0	0	0	0	3	0
<i>Skeletonema</i>	40	20	0	37	0	0	0	0	0	0	0	3	0	0
<i>Thalassiosira</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Thalassiothrix</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Achnanthes</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Streptotheча</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Thalassionema</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Pleurosigma</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Diatom #12</i>	133	20	0	0	0	0	0	0	0	0	0	0	4	0
<i>Stephanophysix</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Diatom #19</i>	8	0	0	0	0	0	0	2	0	2	0	0	0	0
<i>Suriella</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Genus #5</i>	0	1	20	17	8	0	3	5	1	5	351	281	0	1

Appendix Table 5. (Continued).

	NAVY													
	15	16	17	18	19	20	21	22	23	24	25	26	27	28
<i>Asterionella</i>	0	40	0	4	2	13	0	22	0	28	0	0	0	8
<i>Biddulphia</i>	0	5	0	0	0	0	0	0	0	0	0	0	0	0
<i>Ceratulina</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Chaetoceros</i>	0	248	194	21	2	0	0	33	0	0	58	0	2	3
<i>Coscinodiscus</i>	0	0	1	0	2	0	0	0	0	0	1	1	0	4
<i>Ditylum</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Eucampia</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Leptocylindrus</i>	0	0	0	0	0	0	0	0	0	0	0	5	0	0
<i>Licomorpha</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Navicula</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Nitzschia</i>	0	0	0	4	265	0	0	2	0	1	5	1	165	343
<i>Rhizosolenia</i>	0	2	0	0	0	0	0	0	0	0	0	0	8	0
<i>Skeletonema</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Thalassiosira</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Thalassiothrix</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Achnanthes</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Streptotheaca</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Thalassionema</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Pleurosigma</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Diatom #12</i>	0	4	0	0	2	0	0	0	0	0	0	4	0	0
<i>Stephanophysix</i>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<i>Diatom #19</i>	0	0	0	0	0	0	0	0	0	0	0	2	0	0
<i>Suriella</i>	0	0	7	0	0	0	0	0	0	0	0	0	0	0
<i>Genus #5</i>	0	2	0	0	3	2	0	5	0	0	23	2	1	5

Appendix Table 5. (Continued).

	PIER			INLET			NAVY		
	<u>29</u>	<u>30</u>	<u>31</u>	<u>29</u>	<u>30</u>	<u>31</u>	<u>29</u>	<u>30</u>	<u>31</u>
<i>Asterionella</i>	0	0	0	0	0	0	0	0	0
<i>Biddulphia</i>	0	0	1	0	0	0	0	0	0
<i>Ceratulina</i>	0	0	0	0	0	0	0	0	0
<i>Chaetoceros</i>	0	1	5	0	0	0	0	0	17
<i>Coscinodiscus</i>	0	0	4	0	0	0	5	4	0
<i>Ditylum</i>	0	0	0	0	0	0	0	0	0
<i>Eucampia</i>	0	0	0	3	0	0	0	0	0
<i>Leptocylindrus</i>	0	0	0	0	0	0	0	0	0
<i>Licromorpha</i>	0	0	0	0	0	0	0	0	0
<i>Navicula</i>	0	0	1	0	0	0	0	0	0
<i>Nitzschia</i>	12	6	89	3	2	0	6	1	0
<i>Rhizosolenia</i>	44	0	1	1	2	0	0	0	0
<i>Skeletonema</i>	0	0	8	0	25	0	0	0	0
<i>Thalassiosira</i>	0	0	0	0	0	0	0	0	0
<i>Thalassiothrix</i>	0	0	650	0	0	559	0	0	141
<i>Achnanthes</i>	18	0	0	0	0	0	0	0	0
<i>Streptotheaca</i>	0	0	0	0	0	0	0	0	0
<i>Thalassionema</i>	0	0	0	0	0	0	0	0	0
<i>Pleurosigma</i>	0	0	0	0	0	0	0	0	0
<i>Diatom #12</i>	0	0	0	0	0	0	0	0	0
<i>Stephanophysix</i>	0	0	0	0	0	0	0	0	0
<i>Diatom #19</i>	0	0	0	0	0	0	0	0	0
<i>Suriella</i>	0	0	0	0	0	0	0	0	0
<i>Genus #5</i>	0	0	2	0	0	0	0	0	2

Appendix Table 5. (Continued).

<u>Sample</u>	<u>Chlorophyll A mg/m³</u>	<u>Primary Productivity μg Carbon/l/h</u>	<u>Productivity Index</u>
P-0-1	1.5 $\bar{X} = 1.8 \pm 0.9$	22.5 $\bar{X} = 22.3 \pm 2.8$	15.4 $\bar{X} = 13.0 \pm 7.8$
P-0-2	1.7	23.8	13.8
P-0-3	2.06	20.5	9.9
P-5-1	1.7 $\bar{X} = 1.8 \pm 0.02$	26.3 $\bar{X} = 24.0 \pm 4.1$	15.7 $\bar{X} = 13.4 \pm 3.9$
P-5-2	1.8	22.6	12.7
P-5-3	1.9	23.0	11.9
P-10-1	1.8 $\bar{X} = 1.6 \pm 0.04$	10.6 $\bar{X} = 9.7 \pm 1.1$	5.9 $\bar{X} = 6.3 \pm 0.2$
P-10-2	1.4	8.6	6.2
P-10-3	1.5	10.0	6.7
P-20-1	1.3 $\bar{X} = 1.1 \pm 0.05$	5.2 $\bar{X} = 4.2 \pm 1.6$	3.9 $\bar{X} = 3.9 \pm 0.6$
P-20-2	1.0	4.6	4.6
P-20-3	0.9	2.8	3.1
P-50-1	0.8 $\bar{X} = 0.9 \pm 0.02$	3.2 $\bar{X} = 2.0 \pm 1.1$	4.1 $\bar{X} = 2.5 \pm 2.4$
P-50-2	0.8	1.8	2.1
P-50-3	1.1	1.2	1.1
I-0-1	3.2 $\bar{X} = 2.7 \pm 0.3$	9.9 $\bar{X} = 9.1 \pm 5.0$	3.1 $\bar{X} = 3.5 \pm 1.8$
I-0-2	2.8	6.6	2.4
I-0-3	2.2	10.8	4.9
I-5-1	2.4 $\bar{X} = 2.4 \pm 0.1$	13.5 $\bar{X} = 10.2 \pm 3.3$	5.7 $\bar{X} = 4.2 \pm 1.3$
I-5-2	2.1	6.9	3.3
I-5-3	2.8	10.3	3.7
I-10-1	2.2 $\bar{X} = 2.4 \pm 0.2$	15.2 $\bar{X} = 14.0 \pm 3.1$	6.9 $\bar{X} = 5.9 \pm 1.4$
I-10-2	2.4	10.4	4.4
I-10-3	2.6	16.4	6.4
I-20-1	2.5 $\bar{X} = 2.3 \pm 0.2$	6.6 $\bar{X} = 7.2 \pm 3.5$	3.8 $\bar{X} = 3.5 \pm 1.4$
I-20-2	2.0	4.0	2.0
I-20-3	2.4	11.0	4.7
I-50-1	2.5 $\bar{X} = 2.3 \pm 0.2$	9.3 $\bar{X} = 6.8 \pm 2.7$	3.8 $\bar{X} = 3.0 \pm 0.9$
I-50-2	2.2	4.0	1.9
I-50-3	2.2	7.0	3.3

Appendix Table 6. Chlorophyll A, primary productivity, and productivity index for phytoplankton assemblages taken from the PIER and INLET sites under laboratory test conditions; \pm standard deviation.

<u>Sample</u>	<u>Soluble Cu</u>	<u>Total Cu</u>	<u>% Colloidal Cu</u>
P-0-1	1.1 $\bar{X} = 1.3 \pm 0.4$	1.4 $\bar{X} = 1.3 \pm 0.1$	3.7 $\bar{X} = 2.2 \pm 1.3$
P-0-2	1.7	1.3	1.9
P-0-3	1.0	1.3	1.9
P-5-1	1.8 $\bar{X} = 2.7 \pm 0.8$	5.0 $\bar{X} = 5.1 \pm 0.3$	3.0 $\bar{X} = 2.7 \pm 0.3$
P-5-2	3.2	4.9	3.7
P-5-3	3.2	5.4	2.5
P-10-1	5.3 $\bar{X} = 6.2 \pm 1.3$	12.2 $\bar{X} = 10.5 \pm 1.2$	5.2 $\bar{X} = 4.8 \pm 0.3$
P-10-2	-	9.4	4.8
P-10-3	7.1	10.0	4.6
P-20-1	11.0 $\bar{X} = 13.4 \pm 2.6$	5.4 $\bar{X} = 9.5 \pm 9.0$	15.0 $\bar{X} = 14.8 \pm 0.5$
P-20-2	12.9	3.3	15.2
P-20-3	16.2	19.8	14.3
P-50-1	41.4 $\bar{X} = 47.1 \pm 4.9$	52.7 $\bar{X} = 50.5 \pm 6.4$	69.7 $\bar{X} = 54.1 \pm 14.0$
P-50-2	50.0	43.2	42.6
P-50-3	49.8	55.5	49.9
I-0-1	1.9 $\bar{X} = 2.1 \pm 0.6$	5.2 $\bar{X} = 5.0 \pm 2.2$	2.4 $\bar{X} = 3.4 \pm 0.8$
I-0-2	2.8	2.7	3.8
I-0-3	1.7	7.1	3.9
I-5-1	5.6 $\bar{X} = 4.5 \pm 1.3$	8.3 $\bar{X} = 9.8 \pm 2.9$	5.6 $\bar{X} = 6.3 \pm 0.6$
I-5-2	3.0	7.9	6.7
I-5-3	4.8	13.1	6.5
I-10-1	13.8 $\bar{X} = 9.8 \pm 3.5$	16.2 $\bar{X} = 16.3 \pm 0.3$	12.1 $\bar{X} = 12.7 \pm 0.7$
I-10-2	7.0	16.7	12.7
I-10-3	8.7	16.1	13.4
I-20-1	14.8 $\bar{X} = 14.8 \pm 1.5$	3.6 $\bar{X} = 8.5 \pm 6.3$	Contaminated
I-20-2	13.3	6.3	0.8
I-20-3	16.2	15.6	0.8
I-50-1	30.8 $\bar{X} = 40.4 \pm 8.5$	59.5 $\bar{X} = 59.4 \pm 8.9$	41.1 $\bar{X} = 57.2 \pm 18.9$
I-50-2	43.8	68.3	78.1
I-50-3	46.7	50.4	52.3

Appendix Table 7. Soluble, total, and colloidal copper concentrations (ppb) measured in PIER and INLET seawater under laboratory test conditions; \pm standard deviation.

Sample	PIER				INLET				NAVY			
	Temp	Salinity	Tidal Stage	pH	Temp	Salinity	Tidal Stage	pH	Temp	Salinity	Tidal Stage	pH
1	18.5	32.5	2	8.15	22.0	32.5	2	8.15	23.6	32.5	2	8.15
2	16.5	36.0	1	8.27	17.0	36.5	1	8.34	24.5	37.0	1	8.08
3	22.0	33.0	2	8.15	16.0	33.0	2	8.14	21.8	33.8	2	8.02
4	19.5	33.5	2	8.20	21.0	33.7	2	8.17	21.0	34.2	1	8.12
5	20.5	33.7	1	8.11	22.0	33.7	1	8.03	22.0	34.0	1	8.10
6	20.0	33.7	0	8.02	21.5	33.7	2	7.84	No sample			
7	21.0	33.7	0	8.20	22.0	33.8	0	7.76	22.0	33.7	0	7.71
8	21.0	33.5	2	7.67	21.8	33.7	2	7.75	22.0	34.0	0	7.88
9	20.5	33.5	2	8.19	21.0	33.7	2	8.05	22.0	34.2	2	7.88
10	19.0	33.5	2	7.96	20.0	33.6	2	7.84	20.2	34.3	2	8.10
11	16.5	33.5	2	8.05	16.0	33.4	2	8.04	17.2	33.6	2	7.87
12	16.5	33.3	2	8.23	15.5	33.5	2	8.09	16.9	33.9	2	8.05
13	16.9	33.3	0	8.12	16.8	33.5	0	8.21	17.4	33.9	0	8.07
14	17.0	33.5	0	8.13	16.0	33.2	0	8.22	17.0	33.8	0	8.17
15	15.5	33.2	0	8.29	15.2	33.2	0	8.14	No sample			
16	16.0	33.5	2	8.29	16.0	33.2	0	8.20	16.8	33.9	2	8.17
17	13.5	32.8	1	7.93	12.5	32.2	1	7.97	12.8	33.4	1	7.76
18	13.0	30.7	1	7.79	12.0	29.3	1	7.84	13.2	22.2	1	7.69
19	14.5	32.0	0	8.18	14.0	32.4	0	8.11	15.5	31.4	0	8.23
20	15.0	32.4	2	8.21	15.4	32.0	2	8.16	15.4	31.0	2	8.03
21	14.8	32.4	2	8.11	15.0	31.1	2	8.21	No sample			
22	15.5	32.2	0	8.13	15.5	32.2	0	8.22	15.5	31.4	0	8.18

Appendix Table 8. Individual measurements of temperature ($^{\circ}\text{C}$), salinity (ppt), tidal stage (2 = outgoing, 1 = incoming, 0 = changing tide), and pH taken at the PIER, INLET, and NAVY sites from July 1978 through June 1979.

Sample	Temp	Salinity	PIER			INLET			NAVY		
			Tidal Stage	pH	Temp	Tidal Stage	Salinity	Tidal Stage	Salinity	Temp	pH
23	15.8	32.3	0	8.23	16.5	30.9	0	8.20	No sample	15.6	31.5
24	14.8	32.6	2	8.13	15.6	32.2	2	8.22		2	8.20
25	15.2	33.9	2	8.10	16.2	33.7	2	8.18	16.8	34.9	2
26	16.6	32.8	0	8.08	17.2	32.5	0	8.22	17.2	30.3	0
27	16.7	32.7	1	8.13	17.2	32.7	0	8.15	17.6	31.9	0
28	15.5	32.8	0	8.23	17.0	32.7	0	8.15	18.6	31.7	2
29	17.0	32.3	1	8.04	18.0	32.7	1	8.11	19.0	32.1	1
30	17.0	32.6	2	8.26	18.0	32.8	2	8.28	19.0	32.0	2
31	18.8	33.6	1	7.91	19.5	33.6	1	7.94	22.5	33.6	1

Appendix Table 8. (Continued).

Sample	PIER				INLET				NAVY			
	<u>NO₂</u>	<u>NO₃</u>	<u>PO₄</u>	<u>SiO₄</u>	<u>NO₂</u>	<u>NO₃</u>	<u>PO₄</u>	<u>SiO₄</u>	<u>NO₂</u>	<u>NO₃</u>	<u>PO₄</u>	<u>SiO₄</u>
1	1.24	8.5	0.25	14.3	0.17	0.5	0.52	7.8	0.14	0.6	0.88	14.6
2	0.16	0.2	0.62	12.0	0.12	0.5	0.45	10.5	0.70	15.4	0.56	13.1
3	0.11	1.4	0.63	14.1	0.14	0.7	0.63	10.9	0.10	0.8	0.63	12.6
4	0.06	0.6	0.31	4.2	0.14	0.3	0.46	10.3	0.10	2.6	0.69	11.6
5	0.13	0.5	0.67	12.5	0.29	7.6	0.81	11.3	0.24	5.2	1.05	11.3
6	0.33	0.9	0.78	10.4	0.22	0.9	0.81	13.0	0.21	9.6	0.71	3.0
7	0.29	2.5	0.79	9.3	0.22	1.4	0.82	11.2	No sample			
8	0.28	1.8	0.96	11.4	0.19	4.8	0.77	5.1	0.23	1.6	0.91	11.7
9	0.28	21.4	0.58	3.3	0.31	10.2	1.07	8.2	0.23	1.8	0.67	7.9
10	4.95	9400	1.36	8.9	0.43	298	0.87	9.3	0.80	1065	1.52	18.1
11	0.23	1950	1.07	8.9	0.64	102	1.04	13.0	1.34	1690	1.82	17.8
12	0.50	2725	0.70	6.4	5.10	9700	1.31	13.9	1.23	189	2.26	21.8
13	0.32	2010	0.92	10.6	0.67	1445	0.95	8.8	0.81	145	1.61	12.4
14	0.78	70	1.18	14.1	0.69	4.3	1.05	9.4	1.24	12.2	1.97	18.8
15	0.35	4.6	0.67	4.6	0.78	6.3	1.19	11.5	No sample			
16	0.39	5.3	0.88	7.3	0.67	12.5	1.01	11.4	0.81	8.3	1.60	12.5
17	0.50	75	1.31	5.7	0.52	20.6	1.01	6.2	1.10	13.2	1.91	12.6
18	0.49	11.6	1.27	7.8	0.49	13.3	1.27	7.8	0.54	14.7	3.23	17.0
19	0.35	6.4	0.76	2.1	0.40	5.6	0.73	2.8	0.32	3.5	0.85	2.1
20	0.30	9.0	0.77	2.2	0.32	13.3	0.72	3.1	0.36	7.1	1.01	2.5
21	0.28	6.4	0.80	3.3	0.43	34.7	0.85	3.2	No sample			
22	0.30	2.0	0.91	3.5	0.12	1.9	0.42	4.0	0.31	7.3	0.94	3.2
23	0.24	4.8	0.96	3.2	0.21	1.6	0.68	3.0	No sample			
24	0.25	3.5	0.74	3.5	0.21	1.4	0.40	2.7	0.40	5.6	0.95	4.0
25	0.81	22.4	0.96	7.3	0.79	11.6	0.54	5.9	1.07	12.6	1.13	11.4
26	0.52	7.3	0.68	9.3	0.37	3.3	0.55	11.9	0.51	590	0.73	27.0
27	0.39	4.6	0.44	9.9	0.24	1.3	0.52	11.4	0.39	2.5	1.03	23.9
28	0.41	5.4	0.69	7.4	0.38	2.6	0.63	7.7	No sample			
29	0.79	6.9	0.75	10.1	0.87	6.5	0.41	4.2	1.42	7.5	0.93	16.3
30	0.72	9.2	0.80	10.1	0.71	5.8	0.50	4.8	0.75	35.0	0.83	14.8
31	0.44	3.5	1.00	6.4	0.44	13.2	0.71	3.8	0.68	50.0	1.03	5.8

Appendix Table 9. Individual measurements of nitrite (NO_2), nitrate (NO_3), phosphate (PO_4), and silicate (SiO_4) measured in seawater samples collected from the PIER, INLET, and NAVY sites from July 1978 through June 1979. All measurements in $\mu\text{g-at/l}$.

<u>Variable</u>	PIER		INLET		NAVY	
	<u>Mean</u>	<u>S D</u>	<u>Mean</u>	<u>S D</u>	<u>Mean</u>	<u>S D</u>
Temperature	16.9	± 2.4	17.2	± 2.8	18.7	± 3.3
Salinity	33.1	± 0.92	32.9	± 1.23	32.7	± 2.73
pH	8.10	± 0.15	8.09	± 0.14	8.02	± 0.16
Productivity	26.6	± 23.70	41.5	± 20.45	28.3	± 22.20
Chlorophyll A	1.80	± 1.00	3.06	± 1.54	1.67	± 0.82
Productivity index	14.83	± 10.00	15.12	± 7.05	16.16	± 8.28
Soluble copper	0.78	± 0.47	3.33	± 1.45	2.95	± 1.83
Total copper	1.80	± 0.96	8.28	± 3.23	6.64	± 5.49
Colloidal copper	1.48	± 0.79	5.86	± 3.10	4.72	± 4.60
Particulate copper	1.73	± 0.42	2.32	± 0.79	2.35	± 0.91
Diversity index	0.57	± 0.22	0.44	± 0.24	0.44	± 0.26
Nitrite (NO ₂)	0.42	± 0.26	0.41	± 0.22	0.61	± 0.41
Nitrate (NO ₃)	6.63	± 5.93	8.02	± 8.12	10.44	± 12.86
Phosphate (PO ₄)	0.78	± 0.27	0.75	± 0.27	1.19	± 0.63
Silicate (SiO ₄)	7.72	± 3.58	7.94	± 3.55	12.70	± 6.89

Appendix Table 10. Yearly mean values ± standard deviation of all factors assessed at the PIER, INLET, and NAVY sites from July 1978 through June 1979.

